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The Electronic Structure of Bis-cyclopentadienyl Compounds

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The electronic structure of bis-cyclopentadienyl compounds is discussed in terms of molecular orbital theory. The way in which symmetry arguments may be used to facilitate such an analysis is described in some detail.

The purpose of this note is twofold. On the one hand, it is hoped to present a plausible and useful account of the electronic structures attributable to bis-cyclopentadienyl compounds of the transition metals. The current interest in these molecules[1] and their continuous proliferation prompts a rather more detailed examination of their structure than was put forward by either Dunitz and Orgel[2] or by Jaffé.[3] And on the other hand, these systems are beautifully symmetrical. They therefore also offer an opportunity to illustrate in a simple manner, the principles by means of which symmetry arguments are used to elucidate electronic properties.

Since the appearance of Pauling's book,[4] several others have been published, of which that by Coulson[5] is perhaps the most recent. They have served to acquaint primarily experimental chemists with the work that is being done in valence theory. There is, however, a considerable gap that remains to be covered before the current theoretical literature is comprehensible to the student of such books. In particular, the use of group theory in the resolution of problems with high symmetry has only been treated in the later chapters of considerably more exacting texts on quantum chemistry.[6] Whereas it is not, of course, intended to bridge this gap in the present note, it is hoped that the principles underlying the use of symmetry may be illustrated in a straightforward fashion, and that this may aid the experimentalist in deciding for himself the relative merits of proposed electronic structures.

The electronic structure, particularly of ferrocene, has been discussed by several authors.[2,3,7] All are open to some criticism.[1] The approach to be followed here is that of molecular orbital theory, and therefore similar to that of Dunitz and Orgel[2] and of Jaffé.[3] It differs in several respects from these treatments, however, and has been useful in the correlation of more recent information about these bis-cyclopentadienyl compounds. Throughout the analysis, a working rule of least disturbance will be invoked. The local structure of, for example, a cyclopentadienyl group will be disturbed as little as possible so that its considerable resonance energy is not lost. If, as will be shown to be the case, strong primary sources of binding can be found without violating this rule, the structures to which one is led may be regarded as sufficient to describe the molecules, at least to a first approximation. It is then quite possible to discuss second-order terms but in the present instance this is hardly necessary.

(a) The Orbitals of the Metallic Atom or Ion.—For simplicity, we shall confine our attention to the transition metals of the first long period. In their ground states, the atoms of these metals have electronic structures of a common type, namely, $(K)(L)(3s)^2(3p)^6(3d)^m(4s)^n$. Whereas there is only one $4s$ orbital, there are five linearly independent $3d$ orbitals. These may be distinguished by the components of angular momentum $m_l(h/2\pi)$ which they have about some given axis, $0z$ say, where $m_l = 0, \pm 1, \pm 2$. Explicitly, their angular dependence is given by the formulas[8]

$$\begin{aligned} m_l &= \pm 2\colon (15/32\pi)^{1/2}\sin^2\theta\cdot e^{\pm 2i\phi}R(r) = de_{2g}^{\pm} \\ m_l &= \pm 1\colon (15/8\pi)^{1/2}\sin\theta\cos\theta\cdot e^{\pm i\phi}R(r) = de_{1g}^{\pm} \qquad (1) \\ m_l &= 0\colon (5/16\pi)^{1/2}(3\cos^2\theta - 1)R(r) = da_g \end{aligned}$$

The last form of writing will be explained below. In order to show the nature of these orbitals, their contours on the zx-plane (*i.e.*, the two half-planes $\phi = 0, \pi$) have been plotted in Figs. 1–4. The specific example chosen is neutral iron, and the radial functions $R(r)$ were taken from the calculations of Manning and Goldberg.[9] A three-dimensional picture of the moduli of these orbitals (one-electron wave functions) is obtained by ignoring the minus signs wherever they appear and rotating the figures about the z-axis; the contours, on which the absolute values of the orbitals are constant, then appear as surfaces of revolution. For example, the $3d$ orbitals with $|m_l| = 1$ both have moduli which may be represented diagrammatically by the paraboloidal surfaces of Fig. 5. The squares of these moduli, of course, give the corresponding electron densities.

Now these $3d$ orbitals have certain interesting properties. In the first place, suppose we invert them in the origin, namely, the atomic nucleus. That is, let us construct a new set of functions whose values at the point (x, y, z) are the same as those of the original set, evaluated at the point $(-x, -y, -z)$. Then an examination of Figs. 1–4, or an inspection of equation (1) shows that the new orbitals are identical in every way with the old ones: the orbitals are simply reproduced, without change of sign, under the inversion. For this reason, they are said to be "even" (or "gerade") and we use subscripts g in their specification. This is an example of what are known as transformation properties. It is easy to see that the $4s$ orbital is also "even" in this sense.

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[1] G. Wilkinson, P. L. Pauson and F. A. Cotton, THIS JOURNAL, **76**, 1970 (1954), where an exhaustive series of references may be found.

[2] J. D. Dunitz and L. E. Orgel, *Nature*, **171**, 121 (1953).

[3] H. H. Jaffé, *J. Chem. Phys.*, **21**, 156 (1953).

[4] L. Pauling, "The Nature of the Chemical Bond," Cornell Univ. Press, Ithaca, N. Y., 1939.

[5] C. A. Coulson, "Valence," Oxford Univ. Press, Oxford, 1952.

[6] For example, H. Eyring, J. Walter and G. E. Kimball, "Quantum Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1944.

[7] G. Wilkinson, M. Rosenblum, M. C. Whiting and R. B. Woodward, THIS JOURNAL, **74**, 2125 (1952); E. O. Fischer and W. Pfab, *Z. Naturforschung*, **7B**, 377 (1952).

[8] C. A. Coulson, reference 5, p. 27.

[9] M. F. Manning and L. Goldberg, *Phys. Rev.*, **53**, 662 (1938).

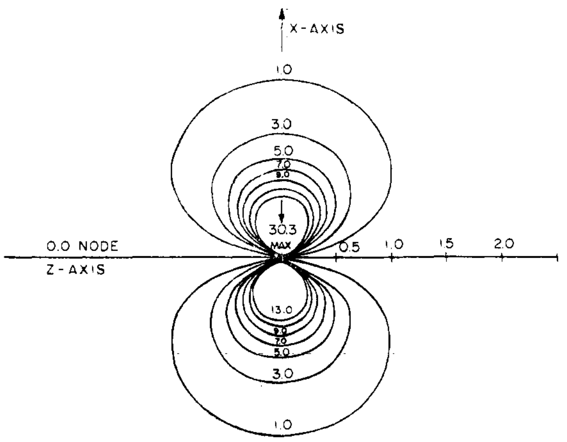

Fig. 1.—Contours on the zx-plane of the iron $3d$ orbital with $m_l = \pm 2$ $(de^{\pm}_{2g})$ (distances along the z-axis in Å. units).

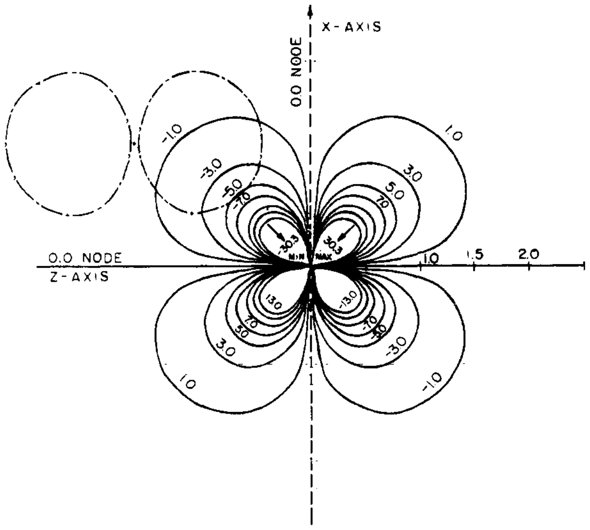

Fig. 2.—Contours on the zx-plane of the iron $3d$ orbital with $m_l = \pm 1$, $(de^{\pm}_{1g})$ (distances along the z-axis in Å. units).

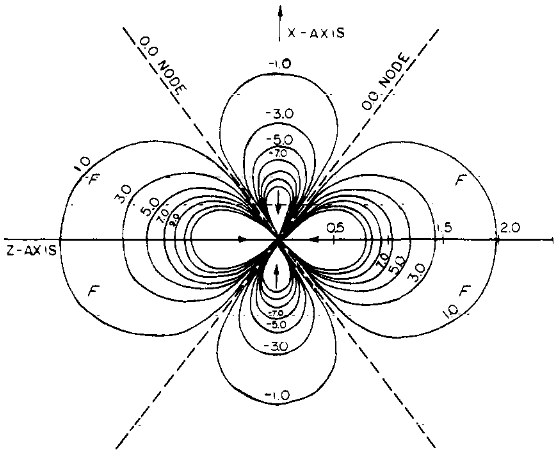

Fig. 3.—Contours on the zx-plane of the iron $3d$ orbital with $m_l = 0$, (da_g) (distances along the z-axis in Å. units).

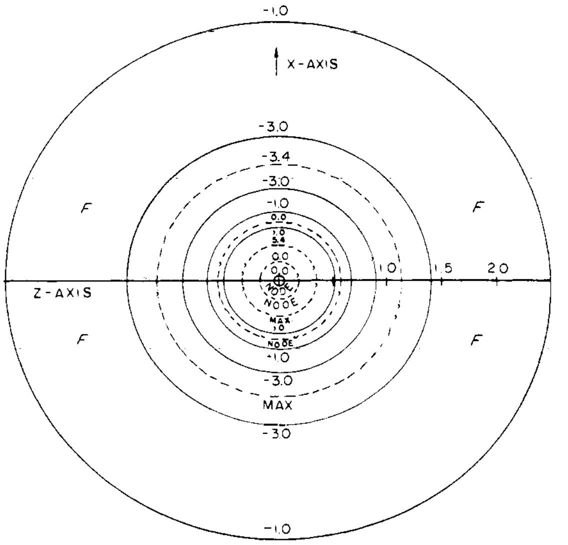

Fig. 4.—Contours on the zx-plane of the iron $4s$ orbital, (sa_g), (distances along the z-axis in Å. units).

As another important example of these properties, consider the effect of a rotation α about the z-axis. That is, construct a new set of orbitals whose values at the point (r, θ, ϕ) are the same as those of the original set at the point $(r, \theta, \phi + \alpha)$. Then it is seen from equation (1) that the new $3d$ orbital with $m_l = \pm 2$ is the same as the old one, apart from a factor $e^{\pm 2i\alpha}$. Similarly, the $m_l = 0$ orbital remains completely unchanged, but the $m_l = \pm 1$ orbitals which arise from the rotation contain the additional factors $e^{\pm i\alpha}$. The $m_l = \pm 2$ orbitals are multiplied by factors which are the complex conjugates, one of another, and are called $de^{\pm}_{2g}$; g because they are "even," e because they are conjugate pairs, and 2 because of the appearance of this term in the appropriate rotation factors $e^{\pm 2i\alpha}$. The $m_l = \pm 1$ orbitals are called $de^{\pm}_{1g}$ for analogous reasons, but the $m_l = 0$ orbital, which remains invariant and, of the $3d$ orbitals, is unique in this respect, is called da_g.[10] The spherically symmetrical $4s$ orbital, which is also "even," remains invariant under the rotation and therefore qualifies for the symbol a_g as well; we call it sa_g. An understanding of these simple transformation properties is of great value in handling problems of high symmetry.

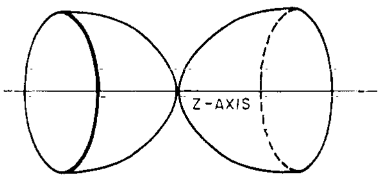

Fig. 5.—Diagrammatic representation of $|de^{\pm}_{1g}|$ contours in space.

Lastly, it is profitable to consider the possibility of a particular kind of hybridization. Suppose we introduce certain external fields which repel electrons in regions of space where the magnitudes of both da_g and sa_g are appreciable. It will be pos-

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(10) The notation has been chosen so as to conform to representations of the point group D_{5d}; for simplicity, however, a_{1g} has been called a_g, since no a_{2g} species occur here. No explicit reference to group theory will be made.

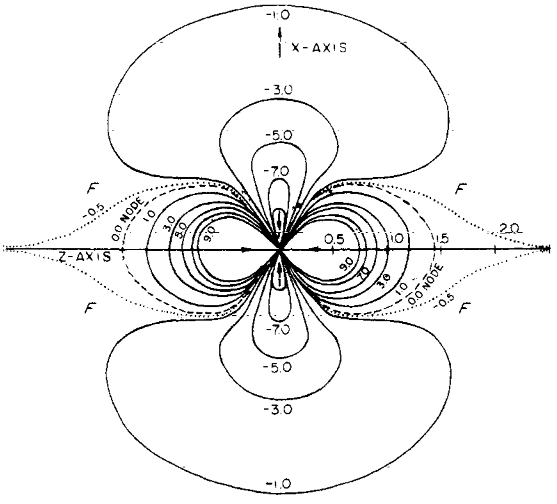

Fig. 6.—Contours on the *zx*-plane of the stable hybrid orbital ha_g in the field *F*.

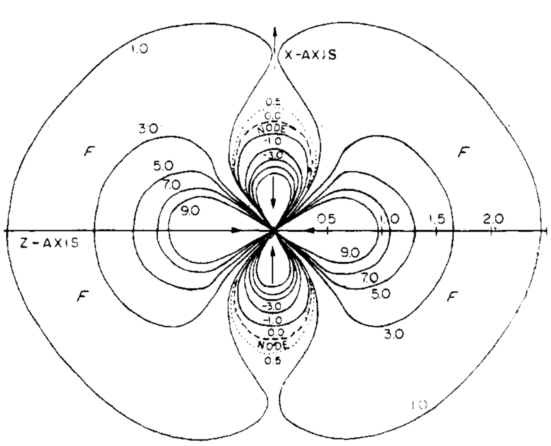

Fig. 7.—Contours on the *zx*-plane of the unstable hybrid orbital ka_g in the field *F*.

sible to construct new metal orbitals of a_g type by linearly combining da_g and sa_g. The interference of these wave functions will increase the values of the hybrid orbitals (and therefore the densities of any electrons they may contain) in some places and diminish them in others. For example, in Figs. 6 and 7 we illustrate, respectively, the two orthogonal hybrid orbitals

$$ha_g = (1/\sqrt{2})(da_g + sa_g) \qquad (2)$$
$$ka_g = (1/\sqrt{2})(da_g - sa_g)$$

It is clear that if the repulsive fields are operative in those regions where ha_g is small, namely, in the areas labeled *F* in the diagrams, then ha_g may be considerably more stable than ka_g and, indeed, more stable than either of the original orbitals, sa_g and da_g. Regarding the field as a perturbation, we see that the effect of the field on the da_g and sa_g orbitals is to mix them in such a way as to produce one orbital, ha_g, which is more stable than either and another, ka_g, which is more highly excited. If there are two electrons of a_g type, therefore, these will be most firmly bound in the hybrid orbital ha_g, and not in either sa_g or da_g. (The precise values of the coefficients determining the amount of hybridization are not in general those given in equation (2)—these were chosen for convenience in illustrating fields like *F*—but must be calculated.) The effect is important whenever the fields *F* are of the same order of magnitude as the difference between the energies of the unperturbed 4*s* and 3*d* orbitals; an inspection of spectroscopic data on, for example, the iron atom, shows that this energy difference is, in fact, quite small.[11]

Other metal orbitals which are reasonably close to, but more highly excited than the 3*d* and 4*s* levels arise from the 4*p* set. It may be shown that these are "odd" (or "ungerade") with respect to the operation of inversion—that is, they change sign. Moreover, that 4*p* orbital with $m_l = 0$ is invariant under a rotation α, whereas the $m_l = \pm 1$ orbitals are multiplied by factors $e^{\pm i\alpha}$. These orbitals are therefore called pa_u, $pe_{1u}^{\pm}$, respectively.

(b) **The Cyclopentadienyl Orbitals.**—We shall now consider the description of an isolated cyclopentadienyl radical. This will be a regular planar system each of whose carbon atoms is joined by σ bonds to its carbon neighbors and to the hydrogen atom with which it is associated.[12] The five electrons which are not yet accounted for are the radical's unsaturation or π electrons. These are assigned to molecular orbitals encompassing all five nuclei and containing the ring system as a nodal plane: the orbitals change sign on reflection in the molecular plane. They are prescribed as linear combinations of the atomic $2p\pi$ orbitals[13]

$$\begin{aligned}
\psi_0 &= \nu_0(\phi_1 + \phi_2 + \phi_3 + \phi_4 + \phi_5) = cpa; \quad \omega = e^{2\pi i/5}\\
\psi_{+1} &= \nu_1(\phi_1 + \omega\phi_2 + \omega^2\phi_3 + \omega^3\phi_4 + \omega^4\phi_5) = cpe_1^+\\
\psi_{-1} &= \nu_1(\phi_1 + \omega^{-1}\phi_2 + \omega^{-2}\phi_3 + \omega^{-3}\phi_4 + \omega^{-4}\phi_5) = cpe_1^-\\
\psi_{+2} &= \nu_2(\phi_1 + \omega^2\phi_2 + \omega^4\phi_3 + \omega^6\phi_4 + \omega^8\phi_5) = cpe_2^+\\
\psi_{-2} &= \nu_2(\phi_1 + \omega^{-2}\phi_2 + \omega^{-4}\phi_3 + \omega^{-6}\phi_4 + \omega^{-8}\phi_5) = cpe_2^-
\end{aligned} \qquad (3)$$

where the ν are normalizing factors, ϕ_r is the $2p\pi$ orbital of atom *r*, and the last form of writing will be explained presently. That the coefficients with which the ϕ_r appear in the molecular orbitals ψ have been well chosen may be verified by solving the requisite secular equation, or otherwise. Since ψ_{-1} is the complex conjugate of ψ_{+1}, and ψ_{-2} the conjugate of ψ_{+2}, the energies of these orbitals are equal in pairs—that is, they fall into two doubly-degenerate levels. More specifically, it may be demonstrated that the energies of the orbitals ψ_0, $\psi_{\pm 1}$, $\psi_{\pm 2}$ are $\alpha + 2\beta$, $\alpha + 2\beta \cos (2\pi/5)$, $\alpha - 2\beta \cos (\pi/5)$, respectively, where α is a constant and β, which is negative, is the usual resonance integral. It appears that ψ_0 is a very strongly bonding orbital, that the $\psi_{\pm 1}$ are less strongly bonding and the $\psi_{\pm 2}$ are quite powerfully anti-bonding. In the ground state of the cyclopentadienyl radical, therefore, the electrons are allotted first to ψ_0 and then to $\psi_{\pm 1}$. There are two possible assignments, $(\psi_0)^2(\psi_{+1})^2\cdot(\psi_{-1})$ and $(\psi_0)^2(\psi_{-1})^2(\psi_{+1})$; both have the same energy, so that the ground state of the radical is doubly-degenerate. (Additional degeneracy also

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[11] R. F. Bacher and S. Goudsmit, "Atomic Energy States," McGraw-Hill Book Co., Inc., New York, N. Y., 1932.

[12] This statement, although perfectly adequate for the purposes of this note, is not strictly true; it will be amplified in a later communication.

[13] C. A. Coulson, reference 5, pp. 238–240.

arises from the two possible orientations of the spin of the unpaired electron in each of these assignments.) The resonance energy of the radical is the difference between the energy of a single structure containing two localized double bonds, $(5\alpha + 4\beta)$, and that of the above allocations, namely, $[5\alpha + 4\beta + 6\beta \cos(2\pi/5)]$. Taking $\beta = -20$ kcal.,[13] this leads to the value of 37 kcal./mole.[14,15]

Now the molecular orbitals in equation (3) also have interesting transformation properties. Consider the effect of a rotation through $2\pi/5$ radians about the fivefold axis of symmetry, perpendicular to the plane of the ring. For example, in place of ψ_{+1} take that function which is obtained from it by replacing atom 5 (and thus ϕ_5) by atom 4 (and thus ϕ_4), 4 by 3, and so on, namely

$$\psi'_{+1} = \nu_1(\phi_5 + \omega\phi_1 + \omega^2\phi_2 + \omega^3\phi_3 + \omega^4\phi_4) = \omega\psi_{+1}$$

since $\omega^5 = 1$. Clearly the effect of the rotation, through an angle $2\pi/5 = \alpha$, say, is to multiply $\psi_{\pm 1}$ by $\omega = e^{i\alpha}$. Similarly ψ_{-1} is simply multiplied by $\omega^{-1} = e^{-i\alpha}$. By the same criterion that we used in discussing the rotational properties of the orbitals of the metals, this pair of orbitals may be called $e_1^{\pm}$; since they are on the cyclopentadienyl ring, we use the more specific notation $cpe_1^{\pm}$.[16] Similarly the molecular orbitals $\psi_{\pm 2}$ acquire factors $e^{\pm 2i\alpha}$ under the rotation, and are therefore referred to as $cpe_2^{\pm}$. The strongly bonding ψ_0 orbital is invariant under the transformation and is called cpa on this account.

Let us now consider a system of two cyclopentadienyl radicals. We suppose that these are sufficiently far apart that the $2p\pi$ orbitals of the one do not overlap the $2p\pi$ orbitals of the other at all appreciably. Moreover, we arrange that the fivefold axes of the two rings coincide; this is to be called the z-axis. In order to fix the signs of the $2p\pi$ orbitals on the one ring (see Fig. 8) relative to those of the other, we choose the point midway between the two rings as the origin and adopt the convention that the negative lobes of the two sets of $2p\pi$ orbitals are directed toward this origin, and therefore toward each other. Finally, we arrange for the two cyclopentadienyl radicals to be *skew*—that is, they will form a pentagonal antiprism. Labeling the carbon atoms of the first ring serially, from 1 to 5, we label those of the second ring 1′ to 5′, such that carbon 1 goes over into carbon 1′, 2 into 2′ and so on, under an inversion in the origin, which is therefore a center of symmetry (see also Fig. 9).

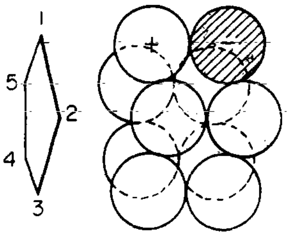

Fig. 8.—A cyclopentadienyl radical.

It is profitable to discuss what happens when the molecular orbitals of the two rings are subjected to this operation of inversion. The molecular orbitals of the first ring Cp_A[16] are called cp_Aa, $cp_Ae_1^{\pm}$, $cp_Ae_2^{\pm}$ and those of the second ring Cp_B are called cp_Ba, $cp_Be_1^{\pm}$, $cp_Be^{\pm}$. Under the inversion, atom 1 and therefore, with our convention of signs, also the $2p\pi$ orbital ϕ_1, go over into atom 1′ and orbital $\phi_{1'}$, respectively. Thus the local molecular orbitals of the first ring, namely, the cp_A's, are transformed into the local molecular orbitals of the second ring by the inversion

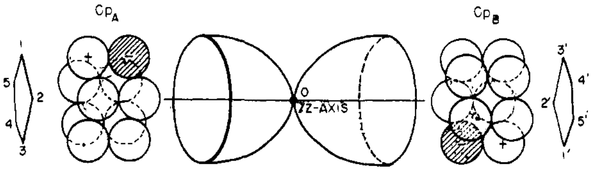

Fig. 9.—The arrangement of the two cyclopentadienyl radicals with respect to the bonding de_{1g} orbitals of the metal.

$$cp_Aa \rightarrow cp_Ba,\ cp_Ae_1^{\pm} \rightarrow cp_Be_1^{\pm},\ cp_Ae_2^{\pm} \rightarrow cp_Be_2^{\pm} \quad (4)$$

And, *mutatis mutandis*, those of the second ring go over into those of the first.

Now it is easy, and convenient, to form linear combinations of the cp_A's and cp_B's which transform into themselves, and not into each other as in (4), under the inversion. The new orbitals, so formed, encompass both rings in this case

$$cpa_g = (1/\sqrt{2})(cp_Aa + cp_Ba),\ cpa_u = (1/\sqrt{2})(cp_Aa - cp_Ba)$$
$$cpe_{1g}^{\pm} = (1/\sqrt{2})(cp_Ae_1^{\pm} + cp_Be_1^{\pm}),\ cpe_{1u}^{\pm} = (1/\sqrt{2})(cp_Ae_1^{\pm} - cp_Be_1^{\pm}) \quad (5)$$
$$cpe_{2g}^{\pm} = (1/\sqrt{2})(cp_Ae_2^{\pm} + cp_Be_2^{\pm}),\ cpe_{2u}^{\pm} = (1/\sqrt{2})(cp_Ae_2^{\pm} - cp_Be_2^{\pm})$$

Using relations (4), it may be shown that cpa_g is indeed "even" with respect to the operation—as the subscript g implies. Moreover, since this orbital contains equal admixtures from cp_Aa and cp_Ba, an electron in the cpa_g orbital spends half its time on any one particular ring, and the remainder on the other. And similarly for the remaining orbitals of (5). The ground state of the system of two non-interacting cyclopentadienyl rings is normally described by the two separate assignments of unsaturation electrons, namely

$$(cp_Aa)^2(cp_Ae_1)^3 \text{ and } (cp_Ba)^2(cp_Be_1)^3 \quad (6)$$

where we have not troubled to distinguish between the e_1^+ and e_1^- orbitals, but tacitly agreed that the doubly-degenerate cpe_1 level may accommodate as many as four electrons, and therefore the three which are indicated. However, if we use relations (5), it may be shown that the three electron assignments each describe states of the composite system

$$(cpa_g)^2(cpa_u)^2(cpe_{1g})^2(cpe_{1u})^4 \quad (7a)$$
$$(cpa_g)^2(cpa_u)^2(cpe_{1g})^3(cpe_{1u})^3 \quad (7b)$$
$$(cpa_g)^2(cpa_u)^2(cpe_{1g})^4(cpe_{1u})^2 \quad (7c)$$

of two rings which, in these simple molecular orbital terms, have the same energy (and, in particular, the same resonance energy) as the specification (6). For, on the average, there are two electrons in cp_Aa and two in cp_Ba, as well as three electrons in each of the levels cp_Ae_1, cp_Be_1. Any one of these assignments, such as (7c) which may contain two unpaired electrons, may therefore be used in order to link the two cyclopentadienyl radicals to the metal

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[14] F. A. Cotton and G. Wilkinson, THIS JOURNAL, **74**, 5764 (1952).

[15] J. L. Franklin and F. H. Field, *ibid.*, **75**, 2819 (1953).

[16] We use the abbreviations Cp for a cyclopentadienyl radical and *cp* to designate orbitals of this radical.

atom, without destroying the resonance energy of either conjugated ring.

(c) **The Use of Symmetry Arguments.**—In the analysis which we have so far undertaken, namely, the orbital description of the fragments which together form the bis-cyclopentadienyl compounds, we have stressed the transformation properties of these orbitals. Before going on to discuss these molecules themselves, we shall explain the reason for this emphasis.

If it is desired to form an electron-pair bond between two atoms or groups by means of electrons in orbital ϕ_w of the one moiety and orbital ϕ_v of the other, then a good criterion of the bonding is given by the overlap of these two orbitals. Now this overlap is gauged by the integral

$$S_{wv} = \int \phi_w^* \cdot \phi_v dv$$

Whenever S_{wv} vanishes, it follows that the orbitals do not overlap, and that they are not suited to binding between the two atoms or groups. On the other hand, if S_{wv} is appreciably different from zero, the overlap is correspondingly large and the incipient binding strong. We shall apply this idea to binding between the orbitals of a metallic atom—which were considered in a—and the group orbitals (5) of the two cyclopentadienyl rings, which were defined and described in b.

The importance of the symmetry properties comes in when we note that the overlap integral S between two orbitals often vanishes identically, because of the way in which the latter transform. They therefore give us an exceedingly powerful method of analyzing the possible sources of binding, or of eliminating the impossible sources. For simplicity, we shall describe a one-dimensional example to illustrate the arguments which are to be used. Let $\phi_w(x)$ be some real function of a single variable x which is "even," that is, $\phi_w(-x) = \phi_w(x) = \phi_w^*(x)$. Also, let $\phi_v(x)$ be some "odd" function of x: $\phi_v(-x) = -\phi_v(x) = -\phi_v^*(x)$. These are shown diagrammatically in Fig. 10. Now let us evaluate the overlap integral

$$S_{wv} = \int_{-\infty}^{+\infty} \phi_w(x)\phi_v(x)\mathrm{d}x$$

Consider the contribution to this integral of increments Δx around the two points $x = -b$, $x = b$. At the former, we have

$$\Delta_- S_{wv} = \phi_w(-b)\phi_v(-b)\Delta x = -\phi_w(b)\phi_v(b)\Delta x$$

since ϕ_w is "even" and ϕ_v is "odd." At the latter

$$\Delta_+ S_{wv} = \phi_w(b)\phi_v(b)\Delta x$$

The sum of these increments therefore vanishes. Moreover, since the whole domain of integration, from $-\infty$ to $+\infty$, may be broken up into pairs of increments of this type, it follows that the value of the complete integral vanishes also. That is, since ϕ_w and ϕ_v transform differently under the inversion in the origin, the overlap between them vanishes identically. When ϕ_w and ϕ_v are both either "even" or "odd," this will no longer be true in general, and these orbitals "overlap."

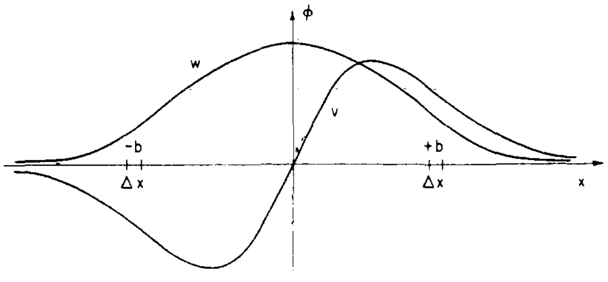

Fig. 10.—To illustrate the use of symmetry arguments.

More generally, it may be shown for the three-dimensional case that whenever ϕ_w and ϕ_v differ in any one transformation property, then the overlap between them vanishes. Thus if ϕ_w acquires the factor $e^{i\alpha}$ under a rotation through $\alpha = 2\pi/5$ radians and is "even" with respect to inversion (*i.e.*, it is of e_{1g}^{+} type), and if ϕ_v is multiplied by $e^{-2i\alpha}$ under the rotation but may also be "even" (of species e_{2g}^{-}), then those two orbitals do not overlap at all. The proof of this theorem requires a more exacting notation, but essentially no different arguments from those which we used in the one-dimensional case above. As an important corollary to this result, it follows that unless the transformation properties of two orbitals are identical, these are not suitable for the formation of electron-pair bonds. This limits the possibilities of binding very considerably and eases the subsequent discussion.

(d) **The Structure of Bis-cyclopentadienyliron (II) (Ferrocene).**—In order to fix our ideas, let us consider the electronic structure of ferrocene. On the extreme right of Fig. 11, we list the orbitals of the isolated iron atom, indicating the symmetries and approximate locations of the $3d$, $4s$ and $4p$ levels. On the left, we show the orbitals of the group of two cyclopentadienyl radicals. Some preliminary calculations, which will be published in full at a later date, show that the cpe_1 orbitals are at about the same level as the iron $3d$ orbitals—that is, their ionization potentials are about equal. As was demonstrated in b, any one of the three assignments (7) describes a state of minimum energy of the two cyclopentadienyl rings (each of whose ground states is degenerate). We choose a particular one of

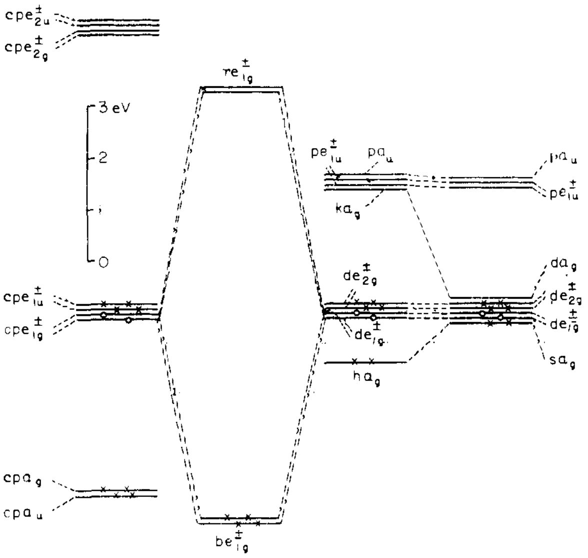

Fig. 11.—Approximate location of molecular, metal and cyclopentadienyl orbitals in ferrocene.

these, namely (7a), illustrating electrons in filled shells by crosses, and unpaired electrons by circles on the diagram. It will easily be seen that (7b) and (7c) are not suitable for binding. There are also several different ways of allotting iron's eight outer electrons to the stable 4*s* and 3*d* orbitals. Only one of these is useful, however, so that we choose to put four electrons into the de_{2g} orbitals, two into the sa_g orbital and one each into de_{1g}^{+} and de_{1g}^{-}.

Now let the two cyclopentadienyl radicals approach the central metal atom in the manner illustrated in Fig. 9. (The only iron orbitals shown in this diagram are rough representations of the de_{1g} orbitals, for reasons which will appear below.)

Before considering the binding possibilities, there is an important effect of Coulomb repulsions which must be considered. When the rings have assumed the positions they occupy in the stable ferrocene molecule, their electrons, which are very strongly bound, have high electron densities in the neighborhood of regions labeled *F* in Figs. 3, 4, 6 and 7. They will powerfully repel electrons in these regions. Accordingly, as was explained in a, the sa_g and da_g orbitals will hybridize to form stable ha_g and unstable ka_g. We may say that the effect of the σ electrons of the two rings is to "polarize" the sa_g and da_g orbitals. The two electrons which we assigned to sa_g for the isolated iron atom, will therefore drop into the favorable hybrid ha_g when the two rings are brought up. The complementary unfavorable hybrid ka_g will probably now lie in the region of the 4*p* orbitals of the iron atom. This reorganization is illustrated, diagrammatically, in the third column of Fig. 11. (The precise location of ha_g and ka_g is difficult to determine. It is only important for our argument that ka_g should not be appreciably more stable than the 4*p* orbitals.)

Finally, we come to consider the nature of the iron–carbon bonding. By the symmetry arguments of c, we need only consider binding between orbitals with the same transformation properties. Moreover, these should contain unpaired electrons. The primary source of the binding must therefore lie between the cpe_{1g} and de_{1g} orbitals. The overlap between these orbitals is not only allowed by symmetry, but also favored by superposition: in Fig. 2, we show a dotted representation of one $2p\pi$ orbital of Cp_A. (More specifically, it is a contour chosen so as just to touch the similar contour on a neighboring carbon atom.) Thus it appears that the ring orbitals cpe_{1g}, which encompass all ten carbon atoms, appreciably overlap the paraboloidal contours of the de_{1g} orbitals (see also Fig. 10). All the prerequisites for strong bonding between them are thus satisfied. Since the energies of the de_{1g} and cpe_{1g} orbitals are also at about the same level, this bonding should not involve charge separation. The net charges on the iron and cyclopentadienyl rings should vanish, in first approximation. Four electrons are therefore involved, two for each Cp-Fe bond.

The bonding orbitals be_{1g}, which in molecular orbital theory will be

$$be_{1g}^{\pm} \approx (1/\sqrt{2})(cpe_{1g}^{\pm} + de_{1g}^{\pm}),$$

are approximately located in the second column of Fig. 11. The complementary antibonding or repulsive orbital

$$re_{1g}^{\pm} \approx (1/\sqrt{2})(cpe_{1g}^{\pm} - de_{1g}^{\pm})$$

is also shown.

There are various secondary types of bonding, which may be considered. For example, the filled de_{2g} orbitals may donate electrons into the vacant cpe_{2g} orbitals. The latter are strongly antibonding in the carbon–carbon sense, and therefore are not inclined to accept electrons—that is, the electronegativity exhibited by the cyclopentadienyl rings is small. Similarly, the filled cpe_{1u} orbitals may formally donate electrons into the vacant pe_{1u} orbitals. However, the cpe_{1u} orbitals are bonding in the carbon–carbon regions, and the electron affinity of iron for 4*p* electrons is low, so this effect will also be small. There may be a little of both occurring simultaneously, leaving no net charge on the rings or on the metal. But this would have to be at the expense of the resonance energy of the cyclopentadienyl rings. Since very favorable binding conditions have already been found, it seems unnecessary to invoke these secondary forces.

This description of the molecule provides a very satisfactory rationalization of the organic reactions of ferrocene, which behaves in many respects like an aromatic system.[17] In our view, each ring has a high local resonance energy, discussed in b and remains uncharged. This is in agreement with the reactivity of the molecule and with the acid dissociation constants of its carboxylic acid derivatives.[17] Since the densities of the bonding iron orbitals are non-directional rotationally but only axially, as shown in Figs. 5 and 9, the two unsubstituted rings should be freely rotating to good approximation. The absence of any nearby unfilled orbitals accounts for the molecule's diamagnetism.

Other Bis-cyclopentadienyl Compounds.—It is interesting to give similar accounts of other neutral molecules like ferrocene, where the central iron atom is replaced by Co, Ni, Cr or other atoms of the transition elements. The energy level diagram will not be very different from Fig. 11 in all these cases, and we may treat the molecules by adding, or subtracting the requisite number of electrons.

The simplest example is bis-cyclopentadienylcobalt(II), where we add one electron. This may go either into one of the 4*p* orbitals or into the relatively unstable ka_g orbital. In either of these cases, of course, it has one unpaired electron (*i.e.*, it is in a doublet state). For bis-cyclopentadienylnickel-(II),[1] on the other hand, two electrons must go into these orbitals. Whether they go, one into ka_g and the other into some 4*p* level, or both into the 4*p* levels, is in many ways immaterial. The proximity of the ka_g orbital energy to that of the 4*p* orbitals will ensure that we shall be left with two singly occupied orbitals whose electrons are in a triplet state with their spins parallel (Hund's principle of maximum multiplicity). In bis-cyclopentadienylchromium-(II) two electrons are removed. If the ha_g orbital is appreciably more stable than the de_{2g} orbitals, both will come from the latter level, leaving one

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(17) R. B. Woodward, M. Rosenblum and M. C. Whiting, THIS JOURNAL, **74**, 3458 (1952).

electron in de^{+}_{2g} and the other in de^{-}_{2g}, so that their spins become parallel, and we have a triplet once again. If the ha_g level is close to the de_{2g} levels, however, one electron will be taken from each and we get another triplet condition. (The ha_g level is certainly not appreciably less stable than de_{2g}, for then it would lose both electrons and leave a diamagnetic molecule—contrary to experience.[18]) More detailed magnetic studies may well be able to settle some of these ambiguities, which are due to our ignorance of the precise location of the ha_g and ka_g levels. However, since these are only concerned with the details of the electronic structure of the metal atom, and do not in any way affect the nature of the metal–carbon bonding, the uncertainties are unimportant in the above instances.

Bis-cyclopentadienylmanganese(II) would be isoelectronic with the ferricinium ion, and arise from the loss of a de_{2g} electron. It is interesting to speculate on the magnetic properties of bis-cyclopentadienyltitanium(II) and -vanadium(II). If, as we may suspect, the ha_g orbital is sufficiently more stable than de_{2g}, in these cases, then $(C_5H_5)_2Ti$, with only two electrons not involved in metal–carbon bonding, would be diamagnetic, both being assigned to the ha_g orbital. However, it is also quite possible that the extra Hund stabilization, which occurs when two electrons can orient their spins parallel to one another, is sufficiently large that one electron goes into ha_g and the other into de_{2g}. The molecule would then be a paramagnetic triplet. If $(C_5H_5)_2Ti$ is diamagnetic, then $(C_5H_5)_2V$ with one additional electron (in de_{2g}) would most probably have only one unpaired electron (doublet state). On the other hand, if $(C_5H_5)_2Ti$ is paramagnetic, it would be supposed that $(C_5H_5)_2V$ has three electrons with their spins all parallel, one each in ha_g, de^{+}_{2g} and de^{-}_{2g} (quartet state).

Throughout, we have regarded, for example, ferrocene as being made up of two neutral cyclopentadienyl radicals and of a neutral iron atom. Moreover, we have shown that this tacit nomenclature reflects the actual charge distribution in the stable molecule. However, since many of the reactions leading to synthesis of bis-cyclopentadienyl compounds occur under ionic conditions, and in view of the oxidation potentials of the compounds, it is in some ways chemically appropriate to regard the metal atom in $(C_5H_5)_2M$ as being in the II oxidation state. Whereas it is not, of course, intended to suggest that the metal has a formal charge of $+2$, this notation is very convenient also in other cases. For example, the name bis-cyclopentadienyltitanium(IV) dibromide refers to the molecule $Ti^{+4}(C_5H^{-}_5)_2(Br^{-})_2$. However, it is better, for structural purposes, to regard this molecule as $[Ti(C_5H_5)_2]^{++}Br^{-}_2$, so that the titanium has two de_{1g} electrons at hand for the metal–carbon bonding—which we consider to be the essential feature of all these bis-cyclopentadienyl molecules. The existence of this particular compound[19] is, in fact, a strong piece of evidence in favor of our picture of the metal–carbon bonding; it can have no more than two electrons available for this purpose.

As a final point, there is no reason why the pentagonal pyramid formed by any one cyclopentadienyl ring and a metal should be a structure unique to bis-cyclopentadienyl compounds. It is quite possible that compounds of a different type, *e.g.*, $[(C_5H_5)M^{n}A_y]X_{n-1}$ where A is a neutral group and X a singly charged anion, can exist. The first examples of such cyclopentadienyl compounds have in fact been made[18]; these are the molybdenum and tungsten cyclopentadienyl carbonyls, (C_5H_5)-$Mo(CO)_5Mo(C_5H_5)$ and $(C_5H_5)W(CO)_6W(C_5H_5)$.

In conclusion, it is hoped that an understandable account has been given of the way in which symmetry arguments may be used to simplify the analysis of the electronic structures which may be ascribed to bis-cyclopentadienyl compounds of the transition elements. More particularly, it has been shown that the essential binding is between the de_{1g} orbitals of the metal and the cpe_{1g} orbitals of the cyclopentadienyl rings, forming two electron-pair bonds. In order to understand the magnetic properties of the compounds, the effect of the electrostatic fields on the da_g and sa_g orbitals of the metal, to produce hybridization, must be considered. Dunitz and Orgel appreciated the predominant role of the e_{1g} orbitals but neglected to consider the *s* or *p* electrons of the metal. On the other hand, Jaffé, in considering all possible combinations of ring orbitals and metal *s*, *d* and *p* orbitals, gave structures whose physical significance it is difficult to understand. Both treatments give erroneous predictions of one sort or another.[1,20]

The author would like to express his cordial thanks to Professors G. Wilkinson and R. B. Woodward for arousing his interest in these molecules.

CAMBRIDGE, MASSACHUSETTS

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(18) G. Wilkinson, THIS JOURNAL, **76**, 209 (1954).

(19) G. Wilkinson, P. L. Pauson, J. M. Birmingham and F. A. Cotton, *ibid.*, **75**, 1011 (1953).

(20) NOTE ADDED IN PROOF.—More recently, in a private communication to the author, Dr. L. Orgel has expressed views which are in substantial agreement with those described in the present note.