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Ionization Potentials of Ferrocene and Koopmans' Theorem. An *ab initio* LCAO-MO-SCF Calculation

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The first ionization potentials of ferrocene have been computed in the LCAO–MO–SCF scheme as the difference of the total energy for the neutral molecule and the positive ion. The corresponding sequence of ionization potentials is found to be

$$\text{I.P.}(e_{2g}) < \text{I.P.}(a_{1g}) < \text{I.P.}(e_{1u}) < \text{I.P.}(e_{1g})$$

in good agreement with the experimental assignment. However, this is different from the sequence of orbital energies for the neutral molecule which is found to be

$$a_{1g}(3d) < e_{2g}(\sigma - \text{Cp}) \sim a_{2u}(\pi - \text{Cp}) \sim e_{2u}(\sigma - \text{Cp}) < e_{2g}(3d) < e_{1g}(\pi - \text{Cp}) \sim e_{1u}(\pi - \text{Cp}) .$$

It is concluded that Koopmans' theorem is not valid for the ferrocene molecule. This is traced to the different extent of the electronic rearrangement which occurs upon ionization, depending on the nature (ligand or metal) of the orbital involved in the ionization process.

Das erste Ionisierungspotential von Ferrocen ist im Rahmen des LCAO–MO–SCF-Verfahrens als Differenz der Gesamtenergie von Molekül zu Ion berechnet worden. Dabei ergibt sich in guter Übereinstimmung mit dem Experiment die Folge

$$\text{I.P.}(e_{2g}) < \text{I.P.}(a_{1g}) < \text{I.P.}(e_{1u}) < \text{I.P.}(e_{1g}) .$$

Sie ist allerdings durchaus von der Orbitalreihenfolge des neutralen Moleküls, die

$$a_{1g}(3d) < e_{2g}(\sigma - \text{Cp}) \sim a_{2u}(\pi - \text{Cp}) \sim e_{2u}(\sigma - \text{Cp}) < e_{2g}(3d) < e_{1g}(\pi - \text{Cp}) \sim e_{1u}(\pi - \text{Cp})$$

ist, verschieden, woraus sich die Nichtgültigkeit des Koopmans-Theorems für Ferrocen ergibt, und zwar läßt sie sich auf den unterschiedlichen Umfang der Elektronenumordnung infolge Ionisation zurückverfolgen, je nachdem, aus welchem MO die Ionisierung stattfindet.

The nature of the bonding in ferrocene $Fe(C_5H_5)_2$ has attracted much interest among both theoreticians and experimentalists. Several semi-empirical calculations have been published [1–7]. Among the experimental techniques, the photoelectron, the electron spin resonance and the electronic absorption measurements have provided useful data for a comparison with theoretical calculations. The lowest two ionization potentials at 6.85 and 7.2 eV in the photoelectron spectrum of ferrocene [8] are due to removal of electrons from the e_{2g} and a_{1g} orbitals which are assumed to be for the greater part localized on the iron atom. One would thus expect from Koopmans' theorem that the sequence of orbitals in ferrocene is

$$a_{1g} < e_{2g}$$

(namely the energy associated with the a_{1g} orbital is larger). However Prins has noted that nothing definite may be said about the order of the a_{1g} and e_{2g} SCF orbitals due to the approximation inherent in Koopmans' theorem (neglect of the electronic relaxation associated with ionization) and to the neglect of correlation energy in the Hartree-Fock approximation [9]. The third and fourth ionization potentials at 8.8 and 9.3 eV in the photoelectron spectrum have been attributed to ionization from the e_{1u} and e_{1g} orbitals which, according to semi-empirical calculations, are essentially ligand π-orbitals. On the basis of ESR measurements for substituted ferricenium cations, it has been concluded that the ferricenium cation FeCp_2^+ has the ${}^2E_{2g}[a_{1g}^2 e_{2g}^3]$ ground state configuration and that the ${}^2A_{1g}[a_{1g}^1 e_{2g}^4]$ configuration belongs to an excited state [9]. From the above studies, Prins has concluded that the order of the highest filled and lowest empty orbitals in ferrocene is [9]

$$e_{1g}(\pi-\mathrm{Cp}) < e_{1u}(\pi-\mathrm{Cp}) < a_{1g}(3d) \sim e_{2g}(3d) < e_{1g}^*(3d)\,.$$

Semi-empirical MO calculations have not reproduced exactly this order [1–7]. Also they have not resolved the problem of the charge distribution in this molecule. Shustorovitch and Dyatkina obtained a positive charge of +0.69 e on the iron atom [1] whilst Dahl and Ballhausen obtained a negative charge of the same magnitude [2]. Simple theoretical arguments have suggested that the electronic structure of ferrocene involves some interaction between the $d_{\pm 1}$ orbitals of the metal and the e_1 orbitals of the cyclopentadienyl rings [10].

We report here some results from an *ab initio* SCF-LCAO-MO calculation including all the electrons. A basis set of 293 gaussian functions (basis sets 12*s*, 7*p*, 5*d* for the Fe atom [11], 8*s*, 4*p* for the C atoms [12] and 3*s* for the H atoms [13]) has been reduced to 85 contracted functions (minimal basis set except for the 3*d* orbitals of Fe which are described by split functions). The bond lengths were taken as Fe–C = 2.106 Å, C–C = 1.43 Å and C–H = 1.12 Å [14]. The hydrogen atoms have been assumed lying in the plane of the carbon rings, although they may be slightly bent out of this plane [14]. The molecule has been assumed in an eclipsed (D_{5h}) equilibrium conformation in accordance with the results of an electron diffraction study in vapor phase [14]. However, all previous studies on the electronic structure of ferrocene have assumed a staggered (D_{5d}) configuration in accordance with the solid state structure. To conform with earlier usage, we adopt in the following discussion the notation of point group D_{5d}.

Orbital energies and LCAO coefficients for the highest occupied molecular orbitals are reported in Tables 1 and 2. The sequence of orbital energies for the ground state of the ferrocene molecule is found to be (Table 2, column 1)

$$\begin{aligned} &a_{1g}(3d) < e_{2g}(\sigma-\mathrm{Cp}) \sim a_{2u}(\pi-\mathrm{Cp}) \sim e_{2u}(\sigma-\mathrm{Cp}) \\ &< e_{2g}(3d) < e_{1g}(\pi-\mathrm{Cp}) \sim e_{1u}(\pi-\mathrm{Cp})\,. \end{aligned}$$

To investigate partially the effect of the basis set used on this sequence of energy levels, we have also performed a set of SCF calculations with different basis sets obtained from the above mentioned one by deleting one or several contracted functions. The corresponding values of the orbital energies are given in Table 2. Except for the interversion of the e_{1g} and e_{1u} levels which are very

Table 1. SCF orbitals for the ferrocene molecule and the ferricenium ion

Orbital	LCAO coefficients[a, b, d]
e_{1u} $FeCp_2$	$0.74\,z(C_1) - 0.26\,z(C_3) - 0.57\,z(C_4)$
$FeCp_2^+\,(^2E_{1u})$	$0.74\,z(C_1) - 0.26\,z(C_3) - 0.56\,z(C_4)$
e_{1g} $FeCp_2$	$0.34\,z(C_1) - 0.63\,z(C_3) + 0.30\,d^1_{yz} + 0.19\,d^2_{yz}$
$FeCp_2^+\,(^2E_{1g})$	$0.33\,z(C_1) - 0.62\,z(C_3) + 0.33\,d^1_{yz} + 0.20\,d^2_{yz}$
e_{2g} $FeCp_2$	$0.26\,y(C_1) - 0.89\,d^1_{x^2-y^2} - 0.13\,d^2_{x^2-y^2}$
$FeCp_2^+\,(^2E_{2g})$	$0.96\,d^1_{x^2-y^2} + 0.07\,d^2_{x^2-y^2}$
a_{2u} $FeCp_2$	$0.52\,z(C_1) + 0.47\,z(C_3) + 0.32\,z(C_4)$
$FeCp_2^+\,(^2A_{2u})$	$0.51\,z(C_1) + 0.47\,z(C_3) + 0.32\,z(C_4)$
a_{1g} $FeCp_2$	$0.29\,z(C_1) + 0.27\,z(C_3) + 0.76\,d^1_{z^2} + 0.08\,d^2_{z^2}$
$FeCp_2^+\,(^2A_{1g})$	$0.99\,d^1_{z^2} + 0.05\,d^2_{z^2}$

[a] Only coefficients greater than 0.2 appear in this table, except for the coefficients of the 3*d* functions.

[b] The notations $y(C_1)$, $z(C_1)$, etc. refer to the appropriate symmetry adapted orbitals[c].

[c] The z axis is the five-fold axis of the molecule. Symmetry with respect to the plane xOz interchange the C_1 and C_2 atoms, the C_3 and C_5 atoms and leave the C_4 atom unchanged.

[d] The notation d^1 and d^2 refer to the split orbitals.

Table 2. Orbital energies (in a.u.) as a function of the basis set

	Basis set			
	I[a]	II[b]	III[c]	IV[d]
e_{1u}	−0.429	−0.435	−0.426	−0.429
e_{1g}	−0.437	−0.426	−0.446	−0.448
e_{2g}	−0.530	−0.507	−0.545	−0.542
e_{2u}	−0.585	−0.585	−0.586	−0.587
a_{2u}	−0.589	−0.592	−0.590	−0.593
e_{2g}	−0.594	−0.593	−0.597	−0.597
a_{1g}	−0.609	−0.599	−0.619	−0.617

[a] No function deleted.

[b] The 3*d* function of lowest exponent is deleted.

[c] The *p* function of lowest exponent (representative of the 4*p* atomic orbital) is deleted.

[d] The *s* and *p* functions of lowest exponent (4*s* and 4*p* atomic orbitals) are deleted.

close, the sequence appears as relatively independant of the basis set used. We may conclude that enlarging the basis set should not change appreciably the sequence of energy levels. It is dubious that the use of a larger basis set, leading to a better wavefunction, will be able to reconcile the computed sequence of orbital energy for the ground state of ferrocene with the "experimental" order of energy levels. The disagreement is emphasized when one realizes that the two highest occupied orbitals in our calculation are predominantly $2p\pi$ ligand orbitals (Table 1) while the two highest orbitals e_{2g} and a_{1g} according to the photoelectron spectrum are predominantly metal orbitals.

We intend to show now that this disagreement regarding the sequence of orbitals is merely the result of a misplaced confidence in the validity of Koopmans' theorem. Experimentally, the sequence of energy levels given [9] for the ground state of the *neutral* ferrocene molecule has been assumed on the basis of the photoelectron spectrum which involves both the positive ion and the neutral parent, of the ESR spectrum of the ferricenium ion and of the absorption spectrum of the ferrocene molecule which involves an excited state besides the electronic ground state. This is based on a widespread conception that experimental information relating to excited states or to a positive ion may be used for the parent neutral molecule in its ground state, for instance that it is possible to equate orbital energies and experimental ionization potentials or to derive a sequence of orbital energies from the observed electronic transitions. Conversely SCF orbital energies are frequently used to predict ionization potentials and this is based on Koopmans' theorem. From the results presented below, it turns out that Koopmans' theorem is not valid for the ferrocene molecule, namely that the sequence of ionization potentials computed as the difference of the energy values for the molecule and the ion is different from the sequence of orbital energies computed for the neutral molecule in its ground state.

We have performed a series of SCF calculations for the ferricenium ion in various electronic configurations, keeping the geometry used for the parent molecule (although the iron-to-ring distance is estimated to be larger in FeCp_2^+ than in FeCp_2 [9]). The computed SCF energies in the restricted Hartree-Fock scheme [15] together with the corresponding ionization energies are given in Table 3. It turns out that the computed sequence of ionization potentials is now

$$\mathrm{I.P.}(e_{2g}) < \mathrm{I.P.}(a_{1g}) < \mathrm{I.P.}(e_{1u}) < \mathrm{I.P.}(e_{1g})$$

in good agreement with the experimental evidence. The computed ionization potential of 8.3 eV, corresponding to removal of one electron from the e_{2g} orbital, is in moderately good agreement with the experimental value of 6.8 eV [8]. There is only a moderate agreement between the computed energies of 23200 cm^{-1} and 23900 cm^{-1} for the charge-transfer transitions ${}^2E_{2g} \to {}^2E_{1u}$ and ${}^2E_{2g} \to {}^2E_{1g}$ of the ferricenium ion compared to the experimental estimates of 16200 cm^{-1} and 20000 cm^{-1} [9]. Nevertheless the agreement obtained with the experimental sequence of ionization potentials is gratifying when one considers the severe limitations of our calculation: use of a limited basis set which is slightly better than a minimal basis set of Slater functions, neglect of correlation energy and assumption of a similar geometry for the positive ions and the neutral molecule.

Table 3. Computed ionization energies

Molecule	Configuration	State	Energy (in a.u.)	Computed I.P. (in eV)	Experimental I.P. (in eV)
FeCp_2	$a_{2u}^2 a_{1g}^2 e_{2g}^4 e_{1g}^4 e_{1u}^4$	${}^1A_{1g}$	−1643.125	–	–
FeCp_2^+	$a_{2u}^2 a_{1g}^2 e_{2g}^3 e_{1g}^4 e_{1u}^4$	${}^2E_{2g}$	−1642.821	8.3[a] (14.4)[b]	6.8
	$a_{2u}^2 a_{1g}^1 e_{2g}^4 e_{1g}^4 e_{1u}^4$	${}^2A_{1g}$	−1642.754	10.1 (16.6)	7.2
	$a_{2u}^2 a_{1g}^2 e_{2g}^4 e_{1g}^4 e_{1u}^3$	${}^2E_{1u}$	−1642.715	11.1 (11.7)	8.8
	$a_{2u}^2 a_{1g}^2 e_{2g}^4 e_{1g}^3 e_{1u}^4$	${}^2E_{1g}$	−1642.712	11.2 (11.9)	9.3
	$a_{2u}^1 a_{1g}^2 e_{2g}^4 e_{1g}^4 e_{1u}^4$	${}^2A_{2u}$	−1642.556	15.5 (16.0)	–

[a] Ionization potential computed as the difference of the energy value for the molecule and the ion.

[b] Ionization potential computed according to Koopmans' theorem.

It is now clear that Koopmans' theorem is not valid for the ferrocene molecule. The reason is to be found in the different extent of the electronic rearrangement which occurs upon ionization, depending on the nature of the orbital involved in the ionization process. For a ligand orbital (e_{1u} or e_{1g} or a_{2u}) there is little electronic rearrangement upon ionization and the ionization potential computed as the difference of the energies for the molecule and the ion is close to the corresponding orbital energy (Table 3). For a metal orbital (a_{1g} or e_{2g}) there is a marked rearrangement upon ionization: while these orbitals include a small amount of ligand orbitals for the neutral molecule, they become nearly pure metal orbitals for the ion (Table 1) and the computed ionization energy may differ from the orbital energy by as much as 6 eV. This difference in the degree of electronic rearrangement is easily understood in terms of charge delocalization. Ionization from the a_{1g} or e_{2g} orbitals leaves a positive charge which is nearly localized on the iron atom, while the positive charge corresponding to ionization from the e_{1u} or e_{1g} orbitals is delocalized on the two cyclopentadienyl rings. The validity of Koopmans' theorem for metal complexes has been previously questionned on the basis of a disagreement between the experimental ionization potentials for tris (β-diketonate) metal complexes and semi-empirical orbital energies for the neutral molecule [16].

We have not considered ionization from the orbitals $e_{2g}(\sigma - \mathrm{Cp})$ and e_{2u}. This would lead to excited states of the ferricenium ion which are probably higher in energy since these orbitals are σ orbitals of the ligands.

The lowest bands in the electronic absorption spectrum of ferrocene have been analyzed as *d–d* transitions [17]. This does not conflict with our conclusion that the two "highest occupied" orbitals[1] in ferrocene are the predominantly ligand orbitals e_{1u} and e_{1g}. The highest occupied orbitals for the $\mathrm{Ni(CN)}_4^{2-}$ ion are ligand π-orbitals with the lowest virtual orbitals being either a π^* orbital of the ligand or a 4*s* or 4*p* orbital of the metal [18–19]. Nonetheless the lowest energy transitions are *d–d* transitions [18]. This may be traced to the fact that the transition energies are not given merely as a difference of orbital energies but include also a Coulomb and exchange term which may be significant enough to determine the sequence of electronic transitions [19–20]. We expect a similar situation in ferrocene and work is now in progress to compute some transition energies.

The following comments are intended to illustrate some details of the wavefunction and electron distribution. From the ESR spectrum, Prins has shown that the e_{2g} molecular orbital is essentially localized on the iron atom with an estimated value of $C_1 = 0.91 \pm 0.03$ for the coefficient of the atomic 3*d* orbital in this molecular orbital. This is in excellent agreement with the value of $C_1 = 0.89$ for the ferrocene molecule and $C_1 = 0.96$ for the ferricenium ion (Table 1). The relative sequence of some orbitals in the ferrocene molecule has been justified on the basis of metal-ligand interactions. According to Prins the bonding e_{1g} orbitals are probably more stabilized by interaction between the ligand π orbitals and the iron 3*d* orbitals than the bonding e_{1u} orbitals by interaction between the ligand π orbitals and the iron 4*p* orbitals [9]. The contribution of the 3*d* atomic

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[1] It should be realized that the concept of highest occupied orbital looses any physical significance if the Koopmans' theorem is not valid.

Table 4. Gross atomic and orbital populations

	Fe	C	H
s	6.00	3.12 (3.04)[a]	0.81 (0.93)
$p_x + p_y$	8.24	2.13 (2.03)	
p_z	4.01	1.06 (1.20)	
d_{xz}, d_{yz}	0.43		
$d_{xy}, d_{x^2-y^2}$	1.86		
d_{z^2}	1.93		
Formal charge	+1.23	−0.31 (−0.27)	+0.19 (+0.07)

[a] The results in parentheses refer to the cyclopentadienyl ion.

orbital to the e_{1g} molecular orbital is indeed larger than the contribution of the $4p$ atomic orbital to the e_{1u} orbital. However this is probably balanced by the bonding character of the e_{1u} orbital with respect to the interaction of the two cyclopentadienyl rings compared to the antibonding character of the e_{1g} orbital (the overlap integral between the $2p\pi$ orbitals of opposite carbon atoms on the two rings amount to 0.067).

Two contracted gaussian functions have been used in this calculation to describe the iron $3d$ atomic orbitals. The first contracted function was taken as the atomic $3d$ orbital for the ion Fe^{2+} [11]. The second function is a gaussian function of exponent 0.15 which does not contribute at all to the atomic wavefunction of the ion Fe^{2+} but which is found to participate appreciably to the e_{1g} orbital of the ferrocene molecule. This is indicative of an orbital expansion upon formation of the complex, associated to a charge transfer from the cyclopentadienyl ring to the iron atom. The results of a population analysis reported in Table 4 for the cyclopentadienyl ion and the ferrocene molecule point to

– a transfer of 0.86 e from the $2p\pi$ orbitals of the rings to the d_{xz} and d_{yz} orbitals of the metal;

– a transfer of 0.24 e from the $2p\pi$ orbitals of the rings to the $4p_x$ and $4p_y$ orbitals of the metal;

– a back-bonding transfer of 0.35 e from the d_{z^2}, $d_{x^2-y^2}$ and d_{xy} orbitals of the metal to the orbitals of the rings.

The net balance is a shift of 0.39 e from each ring to the iron atom.

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Note Added in Proof. The electron spectrum of ferrocene has been analysed by Rabalais *et al.* (J. chem. Physics 57, 1185 (1972)). These authors invoke Koopmans' theorem in conjunction with a sequence of outer molecular orbitals from semi-empirical calculations. They point out that most calculations predict an ordering of $\ldots(e_{2g})^4\,(a_{1g})^2$ for the outer orbitals in contradiction with their experimental result that the ${}^2E_{2g}$ state of ferricenium is below the ${}^2A_{1g}$ state. Our calculation predicts the correct order of these two states.

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