

# The molecular structure of ferrocene

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The vertical iron–cyclopentadienyl distance in ferrocene has been determined using *ab initio* coupled-cluster theory. At the CCSD level, a TZV2P basis set yields a metal–ligand distance of 1.664 Å with all 96 electrons correlated and 1.672 Å with 66 electrons correlated. With 66 electrons correlated at the CCSD(T) level the equilibrium distance is 1.660 Å, in agreement with experiment (1.66 Å). © 1996 American Institute of Physics. [S0021-9606(96)02023-5]

## I. INTRODUCTION

Equilibrium structures of transition-metal compounds are often difficult to calculate accurately using the standard techniques of *ab initio* quantum chemistry. A notoriously difficult example is provided by the metal–ligand equilibrium distance in the ferrocene molecule. Until recently, all attempts at reproducing the correct vertical metal–ligand distance for this molecule had failed. Thus, an early Hartree–Fock calculation by Lüthi *et al.* gave a metal–ligand distance of 1.88 Å,<sup>1</sup> in poor agreement with the experimental value of 1.66 Å.<sup>2</sup> Recently, the Hartree–Fock limit has been established by Klopper and Lüthi at 1.872 Å.<sup>3</sup> Clearly, the Hartree–Fock wave function is incapable of reproducing the equilibrium structure of ferrocene and correlation effects must be accounted for in the description of the electronic system.

At the lowest level, molecular electron correlation effects may be treated by second-order Møller–Plesset (MP2) perturbation theory. However, although experimental geometries are usually quite accurately reproduced at this level, for ferrocene MP2 fails utterly. Thus, a recent accurate MP2-R12 calculation by Klopper and Lüthi (using 1020 Gaussian functions) gives an equilibrium distance of 1.468 Å.<sup>3</sup> The MP2 distance is thus as much as 0.4 Å shorter than the Hartree–Fock distance. Clearly, the MP2 method strongly overestimates the correlation effects in ferrocene. Higher levels of correlation treatments are therefore called for.

The failure of MP2 to account for the correlation effects in ferrocene might be indicative of a multireference problem. However, Park and Almlöf were able to obtain results in reasonable agreement with experiment using the single-reference based MCPF (modified coupled-pair functional) approach.<sup>4</sup> Correlating 66 electrons and using a  $[4s4p3d1f]$  basis on iron,  $[4s3p]$  on carbon, and  $[2s]$  on hydrogen, these authors obtained an equilibrium distance of 1.684 Å, a major improvement on previous attempts. However, the small size of the basis set renders the result of this calculation inconclusive. Therefore, Park and Almlöf carried out additional MP2 calculations on the pair of cyclopentadienyl rings (with a +2 point charge replacing the iron atom) in order to estimate the intramolecular dispersion effects.<sup>4</sup> With such corrections applied, these authors obtained a metal–

ligand equilibrium distance of 1.65–1.67 Å, in agreement with the experiment.

Park and Almlöf note that while the electronic wave function of ferrocene indeed has a single-reference character, there are nevertheless substantial orbital relaxation effects when the wave function is expanded around the Hartree–Fock state. This observation may explain why MP2 fails for this molecule, since it does not take into account the effects of single excitations with respect to the Hartree–Fock reference function. Indeed, an MCPF calculation with single excitations excluded yields a metal–ligand distance of 1.727 Å, compared to 1.685 Å obtained with the same basis but singles included.<sup>4</sup>

Recently, Pierloot, Persson, and Roos have studied the ferrocene molecule using the complete-active-space (CAS) approach.<sup>5</sup> With a basis containing 255 contracted functions— $[6s5p4d2f]$  on iron,  $[4s3p1d]$  on carbon, and  $[2s]$  on hydrogen—these authors obtain a metal–ligand distance of 1.716 Å at the CASSCF (CAS self-consistent field) level and 1.617 Å at the CASPT2 (CAS second-order perturbation theory) level. In these calculations, the active space is constructed by distributing ten electrons among ten orbitals in all possible ways, and 58 electrons are correlated to second order in the CASPT2 calculations. Estimates of the basis-set superposition error (BSSE) yields a metal–ligand distance of 1.643 Å, in reasonable agreement with experiment. Apparently, CASPT2 is capable of handling the correlation effects of ferrocene in a much more satisfactory manner than MP2 since orbital relaxation effects are partly taken care of at the CASSCF level.

From these calculations, a rather clear picture of the problem associated with the correct prediction of the molecular structure of ferrocene may be formed. It is not a basis-set problem nor a multireference problem, but instead one of dynamic correlation. Furthermore, the dynamic correlation effects are not properly accounted for by MP2 theory since single excitations do not enter at this level and the response of the Hartree–Fock orbitals to the fluctuation potential is consequently not taken into account. The accurate calculation of the molecular structure of ferrocene is therefore a quite demanding task, requiring (1) a size-extensive treatment of correlation effects beyond MP2, and (2) a basis

set capable of reproducing the correct equilibrium structure within 0.01 Å, at the very least a polarized triple-zeta basis set.

With the recent development of computational techniques for the integral-direct based coupled-cluster methods, it has become possible to carry out calculations at the CCSD (coupled-cluster singles and doubles) and CCSD(T) (CCSD with corrections for triple excitations based on perturbation theory) levels involving several hundred basis functions.<sup>6</sup> Indeed, in a recent paper, Koch *et al.* have presented calculations on naphthalene involving as many as 548 basis functions.<sup>7</sup> Therefore, it is now possible to calculate the equilibrium structure of ferrocene with reasonable basis sets at the CCSD and CCSD(T) levels. Such calculations are presented in this paper.

## II. COMPUTATIONAL DETAILS

The programs used are described in Refs. 6 and 7. In our current implementation of the direct CCSD method, we cannot calculate molecular gradients. Therefore, during the optimization of the metal–ligand distance we kept the CC and CH bond distances at their experimental values of 1.440 and 1.104 Å,<sup>2</sup> respectively. Also, planarity was assumed for each cyclopentadienyl ligand. These constraints—which have also been imposed in the previous correlated calculations of the ferrocene structure—should not affect the equilibrium metal–ligand distance appreciably.

At equilibrium, the point-group symmetry of a gas-phase ferrocene molecule is  $D_{5h}$ , corresponding to an eclipsed relative orientation of the cyclopentadienyl rings. Unfortunately, due to a deplorable misconception on the part of the authors, the optimization was carried out for the staggered  $D_{5d}$  structure. We believe that this circumstance does not affect the calculated metal–ligand distances significantly. It should be noted that the barrier between the staggered and eclipsed orientations of ferrocene is very small—only about 1 kcal/mol.<sup>8,9</sup> Thus, at room temperature, an appreciable fraction of the ferrocene molecules is found in the staggered conformation. Indeed, in the electron-diffraction determination of the gas-phase structure of ferrocene by Haaland and Nilsson,<sup>8</sup> all possible relative orientations of the rings had to be allowed for in order to arrive at a reasonable fit to the observed radial distribution curves. The experimental metal–ligand distance in ferrocene is thus not associated with the equilibrium orientation alone, but represents an average over all orientations with an appreciable fraction (one-third in the experiment) in the staggered conformation.

The calculations have been carried out using two sets of basis functions. The smaller is the DZP basis of Schäfer, Horn, and Ahlrichs.<sup>10</sup> In this set, there are a total of 241 contracted functions:  $[8s6p3d]$  on iron,  $[4s2p1d]$  on carbon and  $[2s1p]$  on hydrogen. The larger set was obtained by adding a set of  $f$  functions on the iron atom to the TZV2P basis set of Schäfer, Huber, and Ahlrichs.<sup>11</sup> This yields a total of 373 contracted basis functions, distributed as  $[6s5p3d1f]$  on iron,  $[5s3p2d]$  on carbon, and  $[3s2p]$  on hydrogen. The exponent for the  $f$  function is 1.633, as advo-

cated by Park and Almlöf.<sup>4</sup> We refer to this basis as TZV2P+ $f$ .

It should be noted that the TZV2P+ $f$  set is considerably larger than the sets employed by Park and Almlöf<sup>4</sup> and by Pierloot *et al.* in their correlated calculations on the ferrocene molecule,<sup>5</sup> although Park and Almlöf employed an even larger set for estimating the intramolecular dispersion effects at the MP2 level. Our TZV2P+ $f$  basis set differs from those of Park and Almlöf<sup>4</sup> and Pierloot *et al.*,<sup>5</sup> mainly in the treatment of the carbon and hydrogen atoms. Thus, Pierloot *et al.* employ a  $[3s2p1d]$  basis for carbon and  $[2s]$  for hydrogen. Park and Almlöf employ basis sets ranging from  $[3s2p]$  to  $[4s3p]$  on carbon and from  $[2s]$  to  $[2s1p]$  on hydrogen. The need for taking into account basis set superposition error (BSSE) corrections should therefore be less urgent in our calculations than for that of Park and Almlöf and possibly for that of Pierloot *et al.* No such corrections have been applied or estimated in the present work.

Another important issue is the decision as to how many electrons should be correlated in the calculations. In many early attempts at describing the correlation effects of ferrocene, only 18 electrons were correlated. Park and Almlöf argued convincingly against this and chose instead to correlate the entire valence space of 66 electrons, thus freezing only the  $1s$  electrons on the carbon atoms and the  $1s$ ,  $2s$ , and  $2p$  electrons on the iron atom.<sup>4</sup> Pierloot *et al.* correlate only 58 electrons, choosing to freeze also the  $3s$  and  $3p$  electrons on the iron atom.<sup>5</sup> Since the  $3s$  and  $3p$  electrons are as much a part of the valence as of the core electron system, we have chosen to correlate either all 66 valence electrons or the full set of 96 electrons. Although the benefits gained by correlating the core electrons in a standard valence basis set are questionable or even dubious, the all-electron calculations are still useful as an indication of the possible effects associated with truncation of the correlating orbital space. In passing, we note that as many as 30.5 million cluster amplitudes were optimized in the all-electron TZV2P+ $f$  CCSD ferrocene calculations presented in this paper.

Since the geometry optimizations presented in this paper are one-dimensional problems only, we were able to determine the minimum geometry to three decimal places by calculating the energy at three points, suitably selected around the equilibrium geometry. Test calculations indicate that all numbers are accurate to all decimal places given.

## III. RESULTS

The calculations are summarized in Table I, where we have listed the electronic energies obtained for metal–ligand distances of 3.10, 3.16, and 3.20 a.u., together with the equilibrium distances interpolated from these numbers.

Commenting first on the basis-set effects, we notice that in all cases the TZV2P+ $f$  basis leads to a shorter bond distance compared to the DZP basis. The observed contraction is of the order 0.005 Å, and in all cases less than 0.01 Å. Clearly, it is impossible to estimate the basis-set limit accurately based on these calculations. However, it seems unlikely that the basis limit should differ from the TZV2P+ $f$  numbers by as much as 0.01 Å.

TABLE I. Energies (a.u.) at three values of the metal–ligand distance (a.u.) in ferrocene. The equilibrium metal–ligand distance (Å) has been obtained by interpolation from the energies at 3.10, 3.16, and 3.20 a.u.

Method	Basis	Elect.	3.10 a.u.	3.16 a.u.	3.20 a.u.	Min (Å)
CCSD	DZP	66	−1648.615 768	−1648.616 780	−1648.6164 86	1.675
		96	−1648.883 199	−1648.884 070	−1648.8836 93	1.672
	TZV2P+f	66	−1649.020 517	−1649.021 313	−1649.0208 84	1.672
		96	−1649.233 655	−1649.234 082	−1649.2334 15	1.664
CCSD(T)	DZP	66	−1648.717 826	−1648.718 277	−1648.7176 19	1.665
	TZV2P+f	66	−1649.149 913	−1649.150 117	−1649.1492 88	1.660

Comparing the calculations carried out with 66 and 96 electrons, we note that the effect of freezing the core electrons is to increase the distance between iron and the cyclopentadienyl rings. In the TZV2P+f basis, the all-electron calculation yields a bond distance as much as 0.008 Å shorter than in the frozen-core calculation. At the DZP level the shortening is only 0.003 Å. Since our basis set is not sufficiently flexible to describe core correlation effects, these numbers cannot at all be taken as a reliable indication of the effect of core correlation on the calculated metal–ligand distance, but they do indicate that such effects may influence the metal–ligand distance by as much as 0.01 Å. Moreover, this effect appears to affect the distance in the same direction as does basis-set incompleteness. Thus, based on our CCSD calculations, we estimate the CCSD limit to be close to 1.66 Å.

We now consider the effect of higher-order excitations, as estimated perturbatively within the framework of CCSD(T). Clearly, higher-order excitations contract the metal–ligand distance by 0.010 and 0.012 Å at the DZP and TZV2P+f levels, respectively. At the TZV2P+f level, this leads to a final metal–ligand distance of 1.660 Å. The experimental value is 1.66 Å.<sup>8</sup>

#### IV. CONCLUSIONS

We have determined the iron–cyclopentadienyl equilibrium distance of the ferrocene molecule using coupled-cluster wave functions. Employing a triple-zeta valence basis set augmented with a double set of polarization functions (TZV2P+f), we obtain 1.672 Å at the CCSD level and 1.660 Å at the CCSD(T) level. The experimental value is

1.66 Å.<sup>8</sup> All electrons except 1s on the carbon atoms and 1s, 2s, and 2p on the iron atom have been correlated. Both basis set truncation and the neglect of core and core-valence correlation effects appear to increase the calculated separation between the iron atom and the ligands. Further corrections may arise from a complete (unconstrained) optimization of all geometrical parameters as well as the inclusion of relativistic effects. The combined effect of these corrections is expected to be less than a few hundreds of an angstrom in the iron–cyclopentadienyl equilibrium distance.

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