

Issues involved in using MCSCF to investigate catalytic sites involving transition metals

Bryan H. Kim, Carl R.F. Lund*

Chemical Engineering Department, SUNY-Buffalo, Buffalo, NY 14260-4200, USA

Received 20 February 2002; received in revised form 15 April 2002; accepted 6 May 2002

Abstract

Computational quantum chemistry is used in catalysis research in ways that are very different from those in theoretical chemistry research, and as a consequence, standard theoretical chemistry approaches are sometimes not applicable. This paper considers issues associated with the study of heterogeneous catalytic sites and intermediates where single reference theories are not sufficiently accurate, and therefore a technique like multi-configurational self-consistent field (MCSCF) theory must be utilized. The geometric and electronic structure of heterogeneous catalyst sites and intermediates are often not known or are ambiguous, and in such situations, standard theoretical chemistry approaches may be unsuitable. In this paper, the issues involved in using MCSCF for molecular catalysis work are examined. Iron pentacarbonyl and ferric chloride dimer are used as test molecules to illustrate cases where Hartree–Fock (HF) and density functional theory (DFT) both show deficiencies. These test molecules are then used to illustrate how MCSCF can be applied without prior knowledge of geometric or electronic structure and without the benefit of supporting experimental information, to obtain more accurate results than those from the single reference methods.

© 2002 Elsevier Science B.V. All rights reserved.

Keywords: Iron carbonyl; Iron chloride; DFT; MCSCF

1. Introduction

The present paper is motivated by an interest in systems like the zeolite ZSM-5 containing iron cations at exchange sites. These materials have interesting catalytic properties, e.g. [1–4]. They have high catalytic activity for NO_x decomposition, hydrocarbon partial oxidation, and other redox reactions. The authors have been engaged in experimental synthesis and characterization of FeZSM-5 catalysts in reactions like N_2O decomposition [5]. A mechanistic understanding of the catalytic chemistry exhib-

ited by FeZSM-5 is one primary objective, and it would be useful to be able to include the insights that are available through the methods of computational quantum chemistry. Immediately, however, there are unanswered questions: What is the geometric configuration of the site and intermediates? What is the spin multiplicity of the various species? Perhaps most worrisome, are single reference methods capable of accurately describing the sites. One solution to the latter dilemma is to simply use a multi-reference approach like multi-configurational self-consistent field (MCSCF) theory right from the start, but this raises other questions: how does one go about choosing the active space for the MCSCF calculation? What is an appropriate excitation scheme?

* Corresponding author. Tel.: +1-716-645-2911x2211;

fax: +1-716-645-3822.

E-mail address: lund@eng.buffalo.edu (C.R.F. Lund).

The need for usable consistency over absolute accuracy has led to the rise of density functional theories (DFTs) and perturbation theories as the preferred theories for catalysis research. While few would argue that the DFT reliably offers quantitative accuracy on transition metal systems with complex electronic structures, DFT results on transition metal structures have often been quite consistent, and this consistency is achieved without the use of much prior knowledge. Still, some issues remain about using single configuration theories to describe complicated transition metal catalysts such as the FeZSM-5. For example, Hübner et al. [6] investigated iron–sulfur systems using both DFT and high level *ab initio* theories. DFT calculations using B3LYP functionals succeeded in predicting spectroscopic constants, but failed to find the correct energy ordering of low lying electronic states, predicting a low lying excited state to be the ground state. Much more expensive *ab initio* calculations gave quantitatively accurate results on all systems. Somewhat similar work was done on the FeC₂ molecule by Arbusnikov et al. [7]. The DFT calculations (B3LYP) disagree with multi-reference perturbation calculations in the relative energies of the low-lying states of this molecule. These DFT failures are alarming, because they are the kind of failures that could result in a true catalytic intermediate species being eliminated from further consideration.

When using multi-reference methods, theoretical chemists can rely on available information about structure, bonding schemes, etc. when selecting the active space and excitation scheme. In such research, the objective is to gain an accurate, quantitative understanding of an electronic structure for which a qualitative understanding is already available. And since the targets of such investigations are fundamental descriptions of the electronic structures themselves, calculations are usually performed on species that have been extensively characterized experimentally. The qualitative picture of the chemical species gained through experimental work enables the theoretical worker to select sensible parameters for MCSCF calculations. While the calculations are still tricky, the availability of accurate experimental data helps workers in distinguishing failed calculations. However, for zeolite catalyst systems such qualitative understanding often is not available, or is available at a much less detailed level. At the same time, the goal may not be

to obtain the most accurate electronic structure possible, but instead to calculate structures and energies with sufficient accuracy to make correct predictions about reaction pathways. Therein lies the challenge and the motivation for this paper: how can one proceed with such systems and maintain a reasonable expectation of achieving sufficiently accurate results?

This investigation focused on two fundamental issues. The first issue was whether useful MCSCF calculations could be carried out with small basis sets and relatively small active spaces. Ideally, relatively cheap MCSCF calculations should still show marked qualitative improvements over *ab initio* Hartree–Fock (HF) or DFT calculations that are commonly used in preliminary investigations of molecular catalyst systems. However, most quantum chemistry texts state that capturing the correlation energy effectively requires the use of detailed basis sets and large active spaces, making the calculations very expensive and unusable for molecular catalysis research. The second issue is whether it is possible to select meaningful active space and excitation parameters without resorting to experimental information. Likewise, symmetries cannot generally be assumed; rather, it is necessary that the calculation discover any symmetry that may exist. Before jumping to a zeolite system, it seemed prudent to develop an approach and test it using species for which more information is available. Of course, it was equally important to only use this information “after the fact”. To this end, Fe(CO)₅ and Fe₂Cl₆ have been studied, but following an approach that could be directly applied to the study of a zeolite active site about which information was scarce. The study of these two molecules is additionally revealing because it illustrates situations where single reference methods can fail.

Iron pentacarbonyl is a well-characterized low spin molecule for which the effect of the non-bonding d-orbitals upon the metal–ligand bonds is well described by ligand field theory. As such, the overall coordination environment, including bond lengths, can serve as a measure of calculation accuracy. There are other carbonyls of iron, but initial results showed that these behaved in similar manners to the iron pentacarbonyl. Less is known regarding the geometric and electronic structure of the iron chloride dimer, making geometric predictions less reliable for assessing the accuracy of calculations. However, other studies,

to be discussed, suggest that insufficient electron spin density on the ligands can serve as one indicator of a poor calculation. Also, the iron chloride dimer is used in the preparation of some FeZSM-5 catalysts.

2. Methods

Except as noted, GAMESS [8] was used for all ab initio calculations, including restricted HF (RHF), restricted open HF (ROHF), and MCSCF calculations. Molden [9] was used for visualization of orbitals and structures and to prepare the corresponding figures in this paper. Wachter's +f basis set [10] was used on all iron atoms.¹ Relatively cheap basis sets were intentionally chosen for the ligands, in accordance with the purpose of this work; GAMESS' internal TZV basis set was used on chlorine atoms, and GAMESS' internal 3–21 G basis set was used on carbon and oxygen atoms. TZV represents a basis set quality typical of most preliminary work done in the authors' lab. The use of 3–21 G examines whether qualitative insights can still be gained through minimal basis set MCSCF calculations. Virtual level shifting was used to improve convergence properties, and most of the HF runs used the second order SCF orbital optimization (SOSCF) algorithm in GAMESS. (The threshold for starting SOSCF cycles had to be reduced from the default values to obtain convergence.) The symmetry group was specified as C1 for all calculations presented herein. The method for generating initial guesses for the wavefunction for HF calculations is described later.

All of the DFT calculations were carried out using Jaguar 3.5 or 4.0 [11]. In these calculations, B3LYP functionals were used, along with LAV3D effective core basis sets. All calculations were repeated with diffuse and polarization functions to see if addition of more detail into the basis sets would produce better qualitative results. Most of the runs required fully analytic calculations, failing to converge with the pseudo-spectral method available in the Jaguar pack-

ages. Default semi-empirical guesses were used for all the DFT runs presented in this work. Jaguar offers the alternative of defining transition metal fragments with associated electronic states. Some testing was done using that alternative generation method, and the results were the same as when the semi-empirical initial guesses were used. Virtual level shifting was also employed in all Jaguar computations to improve convergence behavior.

MCSCF calculations have a reputation for being difficult to converge. Some means of systematically obtaining meaningful MCSCF convergences was needed. After much testing, the following protocol was evolved. First, an initial guess for the wavefunction was generated from starting species that had no unpaired d-orbital electrons and progressing to a converged HF wavefunction for the species with the correct number of such electrons. (This step was also employed for the HF calculations.) Next, a single configuration MCSCF calculation was performed using the previous wavefunction as an initial guess. This was followed by a preliminary MCSCF calculation with a large active space, but with a simple excitation scheme. The resulting occupation numbers were then used to identify a smaller active space that could be used for the final geometry optimization by MCSCF. The MCSCF wavefunction generated in this preliminary job was used along with the smaller active space in the final geometry optimization calculations. The remainder of this section provides additional details about these steps. This protocol is somewhat reminiscent of the approach used by Lüthi et al. [12] in an early contracted configuration interaction calculation on iron compounds. It is most important that there was no "manual" generation of the active space that relied on the availability of experimentally obtained orbital information. It is also important that this protocol was used in an identical sequence of steps for all jobs. As much as possible, these steps were tested for suitability on larger zeolite cluster models.

For an HF calculation, quantum chemistry codes often use extended Hückel theory or some other semi-empirical theory to generate initial guesses for their wavefunctions. The assumptions of these theories are acceptable for systems with empty or full d-orbitals, but they can fail for transition metal systems with partially occupied d-orbitals. Nonetheless, modern quantum chemistry codes are relatively

¹ Pacific Northwest Labs, EMSL Basis Set Library, Basis sets were obtained from the Extensible Computational Chemistry Environment Basis Set Database, Version 4/22/01: as developed and distributed by the Molecular Science Computing Facility, Environmental and Molecular Sciences Laboratory which is part of the Pacific Northwest Laboratory, P.O. Box 999, Richland, WA 99352, USA (funded by the US Department of Energy).

robust, and HF/DFT calculations will usually converge for small clusters like iron pentacarbonyl and iron chloride dimer without too much trouble. Larger clusters do not behave so benignly; a few trial calculations with much larger zeolite models that contain iron dimers showed extremely poor HF convergence behavior from the semi-empirical guesses. Simply resorting to more powerful convergence algorithms proved futile. Exacerbating this poor convergence performance was the fact that converged HF wavefunctions were needed as the guesses for MCSCF calculations. MCSCF calculations have to be started from high-quality HF wavefunctions, so it was important to ensure that HF wavefunctions represented the best results that could be generated with the HF theory.

These failures were avoided in this work by initially altering the nuclear charge and the number of electrons in such a way as to preserve the expected d-orbital splittings while eliminating the open shell d-orbital electrons. That is, iron pentacarbonyl is expected to be d^8 , with a formal oxidation state of 0 and with two sets of degenerate d-like orbitals. Therefore, the nuclear charge was reduced by four, and four electrons were removed, effectively turning the iron atom into a titanium atom, as shown in Fig. 1. This step represents the greatest degree of worker intervention needed for the MCSCF calculations presented in this paper. Since the worker constructed the model in the first place, the coordination environment of the cation in the model is well known to the worker. The use of some qualitative d-orbital theory should always permit prediction of reasonable d-orbital splittings. While the nuclear and electronic charges were those of titanium, an iron basis set was used. This pseudo-titanium pentacarbonyl cluster gave absolutely no convergence problems with

default settings, resulting in a good trigonal bipyramid structure under geometry optimization, without any symmetry constraints. The converged SCF wavefunction was then used as the initial guess in a calculation where the nuclear charge on the transition metal was increased by one or two and a corresponding number of electrons was added, and another single point calculation was carried out. In this way, the nuclear charge and the corresponding number of electrons were increased until the true iron atom was restored.

For Fe_2Cl_6 , the spin state was not known with certainty. Based on the fact that solid state $FeCl_3$ is found to be high spin, a ferromagnetic spin coupling was assumed. The possibility of different spin states was examined by a number of single point calculations that differed only in their spin multiplicity. With this assumption, the iron atoms in Fe_2Cl_6 are expected to be in +3 oxidation states, leaving five high spin d-level electrons on each atom; all of the electrons at that level were removed, leading to a pseudo-scandium species. Again, the iron basis sets were used. As with the carbonyl calculations, the converged wavefunctions were then used as the initial guesses for subsequent single point energy calculations that increased the nuclear charges and the number of electrons, until Fe_2Cl_6 was recovered. As mentioned already, HF convergences could be obtained on iron pentacarbonyl or ferric chloride dimers without these artifices, but the ultimate aim of the study was to treat zeolite models, so this more robust method for obtaining the initial wavefunction was employed.

If the wavefunctions generated in this way were used directly as initial guesses for an MCSCF calculation, it was sometimes observed that the MCSCF electronic energy was greater than that of the HF reference. This problem was traced to the Davidson

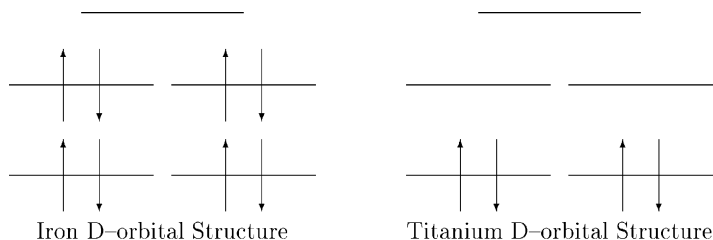


Fig. 1. Scheme for removing electrons. Iron pentacarbonyl's trigonal bipyramid structure is known to split the d-orbitals according to these diagrams. Preserving this d-orbital splitting requires that four electrons be removed. If the energy spacing of the orbitals is close enough, the four remaining electrons realign in a high spin configuration. However, the restricted nature of the calculation enforces the spin pairings.

diagonalization process, and was solved by including a single configuration MCSCF orbital calculation stage right after the HF calculations. This is a rather trivial, albeit somewhat time consuming, transformation; without fail, the converged MCSCF single configurational energy was identical to that of the reference HF energy. Lüthi et al. [12] mention approximating a single configurational MCSCF calculation step in order to generate the set of natural orbitals necessary to make profitable use of configuration interaction methods in their investigation of iron carbonyls.

Having thus produced a suitable reference orbital set for an MCSCF calculation, the next stage was selecting a meaningful active space. A preliminary MCSCF calculation was carried out using the largest possible active space at the expense of simplifying excitations schemes. This preliminary MCSCF calculation served to refine the orbitals from the single configuration MCSCF calculation. Generally, a single and double (CISD) excitation scheme was used for the preliminary calculations, since CISD is the sim-

plest excitation scheme that captures a large amount of correlation energy. It should be noted that in the MCSCF calculations used here both the molecular orbitals making up the reference wavefunction and the coefficients multiplying the different excited populations were optimized. The active space was as large as possible within the limit of available computer memory.

The occupation numbers of the orbitals resulting from the preliminary MCSCF calculation offer trivially simple and chemically meaningful parameters for determining the level of participation of specific orbitals in the configuration interaction, that is, for selecting the active space to be used in the final MCSCF calculations. A fully doubly occupied orbital that gives up very little electronic density to excitations does not need to be included, nor does a completely empty virtual orbital. Figs. 2 and 3 show the occupations of relevant orbitals from the preliminary MCSCF calculation on iron pentacarbonyl. (Note, in these figures and elsewhere in this text, we use HOMO and LUMO to denote the higher occupied and lower unoccupied

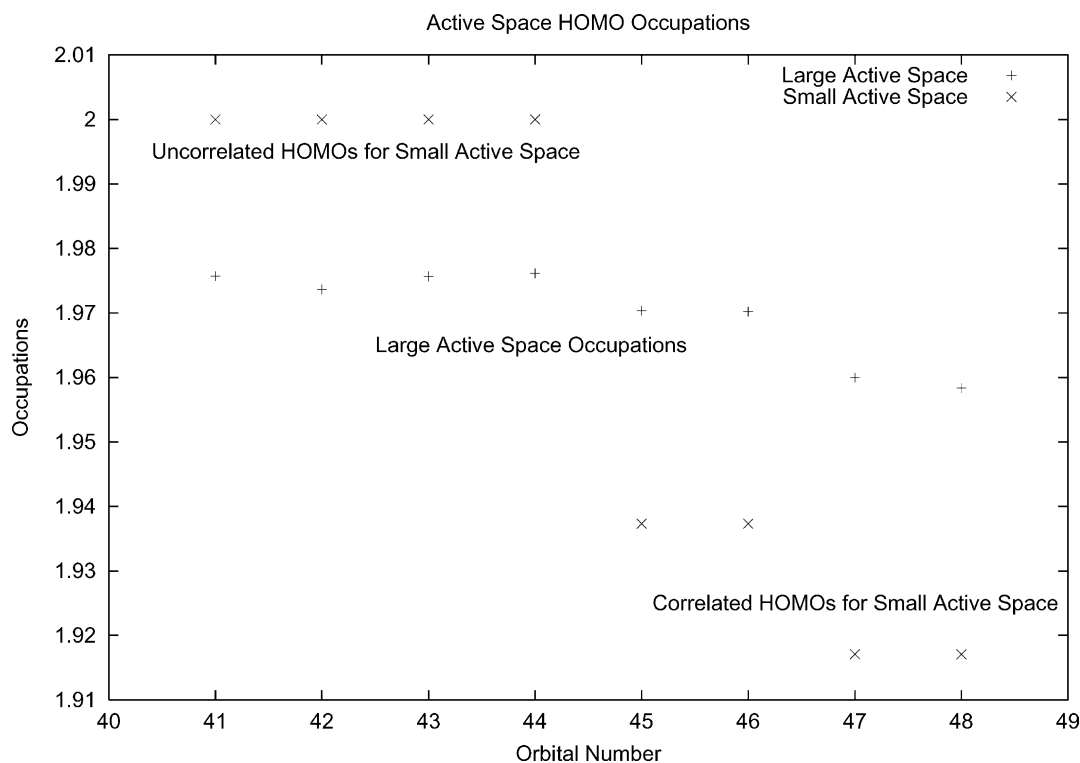


Fig. 2. HOMO occupation numbers from the preliminary and final MCSCF calculations for $\text{Fe}(\text{CO})_5$.

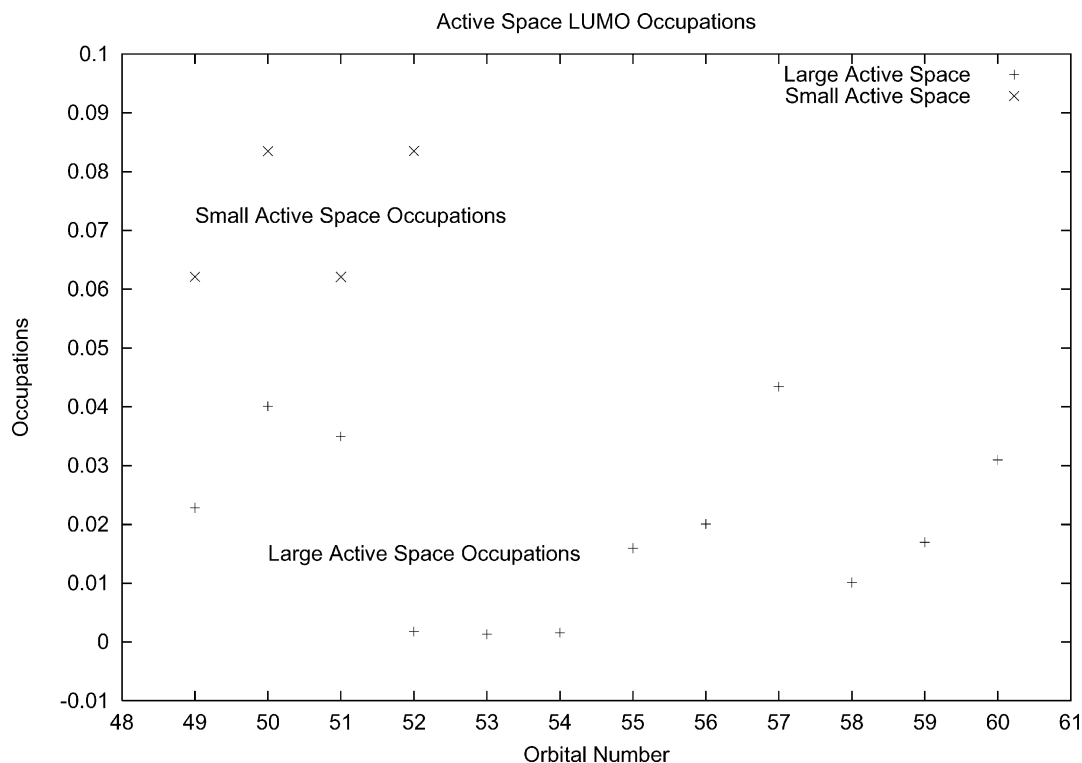


Fig. 3. LUMO occupation numbers from the preliminary and final MCSCF calculations for $\text{Fe}(\text{CO})_5$. Note that renumbering prior to the final MCSCF calculation converted orbital 57 into orbital 52.

orbitals, even though these acronyms properly refer to the single highest occupied and lowest unoccupied orbital.) Among the occupied orbitals (Fig. 2), orbitals 47 and 48 form a group that gave up the greatest amount of electronic density, orbitals 45 and 46 form a second group that gave up somewhat less electron density, and orbitals 41–44 arguably form a third group which gave up even less electron density. Among the virtual orbitals (Fig. 3), orbitals 49–51, and 57 form a group that accepted the largest amount of electron density, followed by orbitals 55, 56, 58–60 which form an intermediate group and orbitals 52–54 which accepted the smallest amount of electron density. The first two groups from the occupied orbitals (45–48) and the first group from the virtual orbitals (49–51, and 57) were selected for the active space for the final MCSCF calculations for iron pentacarbonyl. It should be noted that the orbitals must be re-ordered for the final MCSCF run so that orbital 57 becomes orbital 52.

The iron chloride calculations were qualitatively different from the carbonyl calculations at this stage, although the same procedures were used successfully. One difference involved the necessity of examining two possible geometries: a planar ring and a puckered ring. Another was that three types of orbitals had to be included in the active space: doubly occupied orbitals, singly occupied high spin HOMOs, and virtuals. The preliminary calculations required active spaces that were too large for the available computers' memories. Therefore, the preliminary active space calculations were done in two stages; the first stage included more occupied orbitals, and the second stage included more virtuals. Even after the active space was reduced for the final calculation, it was still too large for a comprehensive excitation scheme. Therefore, a CISD excitation scheme was retained for all stages of this calculation. Examination of the occupation numbers shown in Figs. 4–6 revealed that there was much less electron migration from the occupied orbitals to the

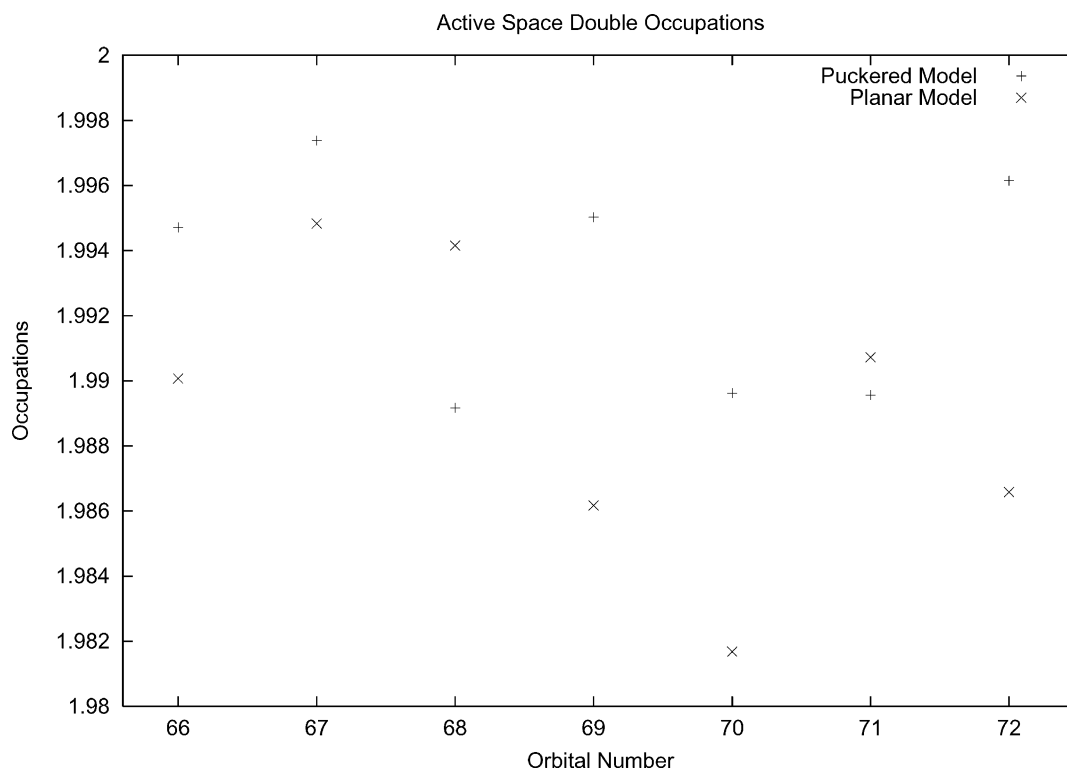


Fig. 4. Occupation numbers for the doubly occupied orbitals from the preliminary MCSCF calculations for the planar ring and puckered ring Fe_2Cl_6 structures.

virtual orbitals (the electron density shift is an order of magnitude less than that seen in Figs. 2 and 3). In addition, the orbitals cannot be grouped as clearly as in the iron pentacarbonyl case.

The occupation numbers for the singly occupied HOMOs for the puckered geometry are very interesting, because most of them are almost exactly one. Such exactness was unexpected; it almost seems like these did not participate very much in excitations, and

the reason is unclear. Even though there is little electron density migration from the occupied orbitals into the virtuals, there is energy stabilization, as can be seen in Table 1, where final results are listed. The magnitude of the deviations shown in Fig. 5 for the planar ring cluster occupations is typical. The final selection of an active space in this case was somewhat more arbitrary. Finally, after re-ordering the orbitals appropriately, geometry optimization was performed by

Table 1

Comparison of results of calculations on iron chloride using various levels of theory (Cl(t): terminal chlorine; Cl(b): bridging chlorine)

Method	Fe–Cl(t) average length (Å)	Fe–Cl(b) average length (Å)	Cl(t)–Fe–Cl(t) angle (°)	Cl(b)–Fe–Cl(b) angle (°)	Energy (Hartrees)
Experimental puckered [30]	2.127	2.326	124.3	90.7	–
Experimental planar [30]	2.127	2.326	122.1	92.9	–
ROHF planar	2.204	2.427	122.45	85.70	–5282.12953
DFT planar	2.165	2.386	117.16	90.99	–3008.54312
MCSCF planar	2.201	2.425	121.78	86.33	–5282.27404
MCSCF puckered	2.199	2.432	121.44	84.78	–5282.43270

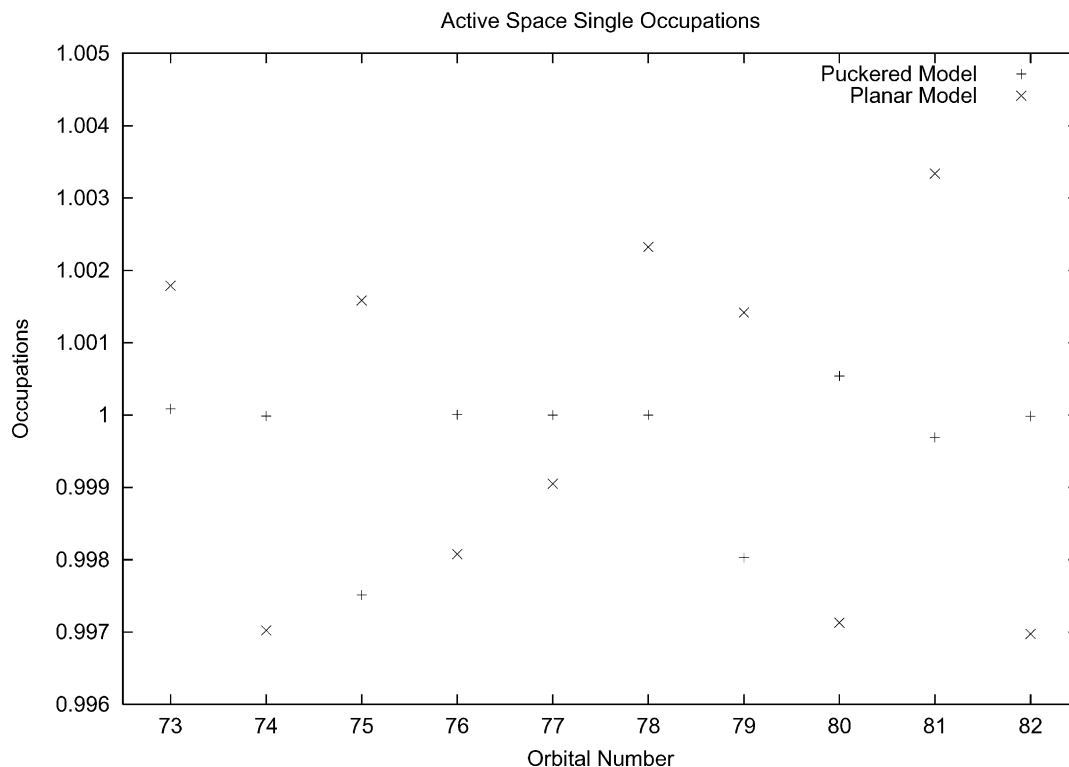


Fig. 5. Occupation numbers for the singly occupied high-spin HOMOs from the preliminary MCSCF calculations for the planar ring and puckered ring Fe_2Cl_6 structures.

MCSCF using the active space chosen on the basis of the preliminary MCSCF. A CISD excitation scheme was used, and the geometries converged easily with default convergence algorithms and tolerances.

3. Results and discussion

Among the first successful computational treatments of iron compounds was that of Lüthi et al. [12]. Having noticed that the HF theory performed very poorly for transition metal carbonyls, they resorted to contracted configuration interaction calculations involving natural orbitals using a procedure quite similar to that used in the present work. Lüthi et al. imposed C_{2v} symmetry and used a very large number of configurations with fairly high-quality basis sets. By doing so, they obtained more reasonable axial bond lengths than had been achieved in prior computations. Yamamoto et al. [13] also reported reasonable

bond distances that compared well to complete active space self-consistent field calculations, but the overall performance of their RHF theory calculations was quite poor. Later, Yamamoto et al. [14] extended their work on Fe–O bonds using small basis set MCSCF calculations. They obtained interesting qualitative results that captured meaningful improvements in electron density localizations compared to RHF results, even though the basis sets that they used were almost minimal. This is one of very few instances of anyone attempting a minimal basis set MCSCF calculations that the authors were able to find in literature. They refined their work later with more rigorous calculations [15]. Their later work demonstrated that the earlier work with minimal basis sets was still instructive.

Ghosh et al. [16] used local DFT to treat mononuclear iron systems very similar to the ones treated by Yamamoto et al. Their calculations were spin unrestricted, and von Barth–Hedin exchange–correlation

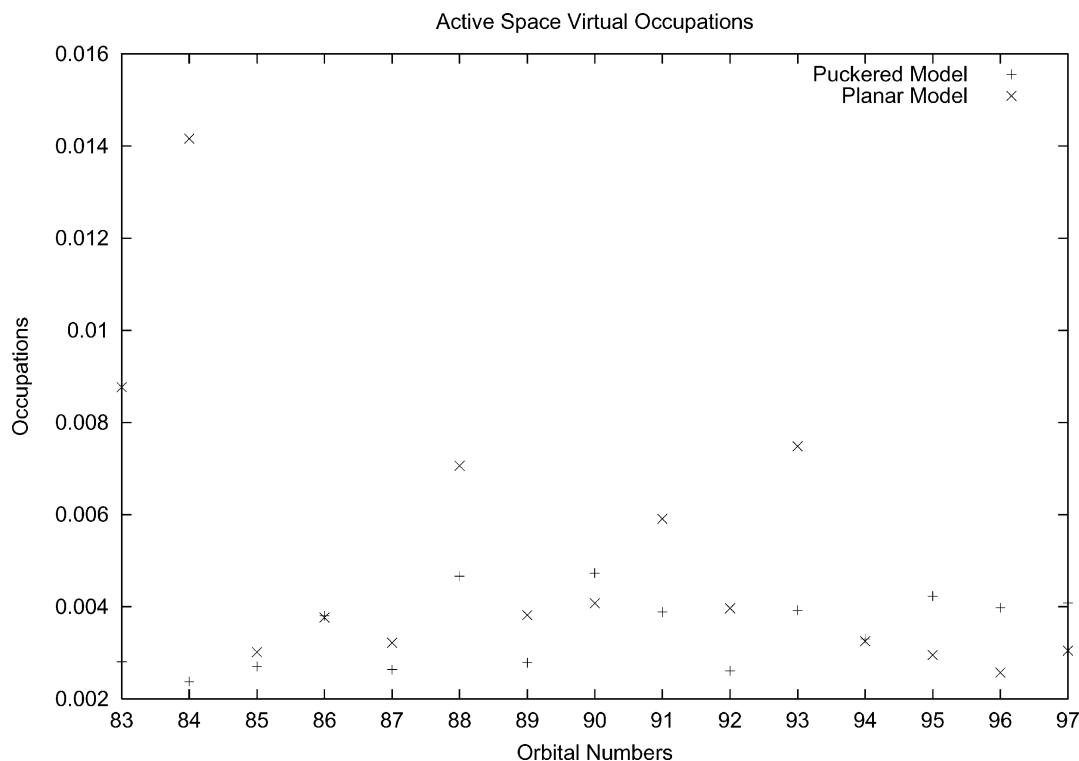


Fig. 6. Occupation numbers for the correlated virtual orbitals from the preliminary MCSCF calculations for the planar ring and puckered ring Fe_2Cl_6 structures.

functionals were used. The results were similar to those of Yamamoto et al., including reasonable spin density distributions across atoms. They noted that DFT, which is formally a single reference theory, reproduced spin density results that hitherto had only been obtained with multi-reference calculations.

Barnes et al. [17,18] applied modified pair coupled-functional theory in order to carry out size extensive calculations on iron and chromium carbonyls. Enlarging the basis sets used on the carbonyl ligands reduced the metal–carbon bond distances significantly. More detailed MCSCF calculations were carried out on the same molecule by Marquez et al. [19]. Million-configuration runs were carried out in order to generate the reference wavefunctions from which single and double excitations into all the virtual orbitals were carried out. Excellent quantitative agreements were obtained for different ligand field state and ionic state energies, but the authors acknowledged the difficulties of carrying out such an

intensive set of calculations, concluding that this approach was “far from being systematic”. A very similar set of calculations was carried out by Rubner et al. [20] in their investigation of the excited states of iron pentacarbonyl.

The present investigation began with HF calculations using a trigonal bipyramidal geometry, consistent with experiment, Table 2. However, the molecular geometry was specified so that one of the equatorial ligand bonds formed the z -axis instead of the natural z -axis. A geometry optimization on pseudo-titanium pentacarbonyl retained the trigonal bipyramidal structure and the equatorial z -axis ligand remained an equatorial ligand. Of course, bond lengths were longer than those of true iron pentacarbonyl. From the result, a trigonal bipyramidal true iron pentacarbonyl single point calculation was converged using the procedure described previously. This served as a starting point for an RHF geometry optimization and for an MCSCF geometry optimization.

Table 2

Comparison of results of calculations on iron pentacarbonyl using various levels of theory (TBP: trigonal bipyramid; SP: square pyramid)

Method	Axial length (Å)	Equatorial length (Å)	Axial–equatorial angle (°)	Energy (Hartrees)
Experiment [31]	1.811	1.803	89.47/90.38	–
DFT (TBP)	1.815	1.810	90.00	–690.35055
DFT (SP)	1.815	1.824	103.45	–690.34725
RHF (SP) ^a	1.905	1.962	105.70	–1822.74620
RHF (TBP)	1.937	1.885	90.00	–1822.74121
RHF (Ti-TBP)	2.081	2.200	90.03	–1407.19029
MCSCF (TBP)	1.937	1.885	90.00	–1823.00420
MCSCF (SP)	1.877	1.913	102.79	–1822.99810

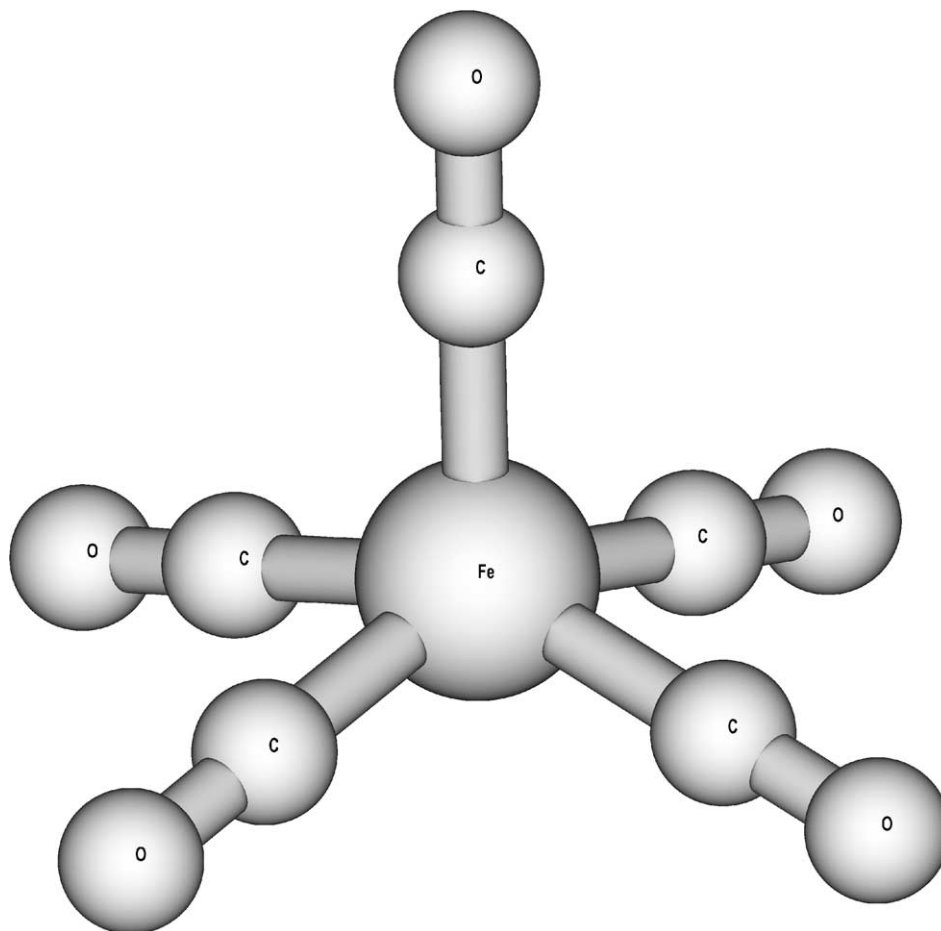
^a Single point calculation using the final structure determined via the MCSCF geometry calculation.

Fig. 7. Square pyramidal geometry identified as a minimum energy structure in HF, DFT, and MCSCF calculations. It is the only minimum energy structure found using HF; DFT and MCSCF identified a trigonal bipyramidal geometry as being lower in energy.

When the RHF geometry optimization was performed, the final structure was as shown in Fig. 7, a square pyramid. The ligand that had started as the equatorial z -axis became the unique ligand in the square pyramid. In contrast, in the MCSCF geometry optimization that used the same trigonal bipyramid as a starting point, the final structure remained a trigonal bipyramid. Similarly, a DFT calculation also found a trigonal bipyramid as the optimal structure. The final geometries and energies are summarized in Table 2. The MCSCF trigonal bipyramid structure has bond lengths that are too long. Barnes et al. [17,18] noticed that ligand bond lengths were too long on these systems when minimal basis sets were used, so this is probably an effect of the minimal basis set used for the carbonyls in the present work. The MCSCF bond lengths are better than the RHF results with the same minimal basis set. The perfect axial–equatorial ligand angle is very satisfying, since it was obtained with no imposed symmetry, bad axes, minimal basis sets, a small active space and a simple excitation scheme. It is also interesting to note that when an RHF single point calculation was carried out on the final trigonal bipyramid from the MCSCF geometry optimization, the RHF energy of the trigonal bipyramid was slightly greater than the RHF energy of the square pyramid.

Returning to the square pyramid, a DFT geometry optimization and an MCSCF geometry optimization were performed starting from the square pyramid. In both cases, the final structure remained a square pyramid, but its energy was higher (in both cases) than the energy of the trigonal bipyramid. Note that these DFT calculations were not minimal basis set calculations; they used the more detailed ECP basis sets with diffuse and polarization functions. DFT appears particularly well suited for iron carbonyls. The work by Jacobson and Ziegler [21] on derivatives of $\text{Fe}_2(\text{CO})_9$ produced bond lengths accurate to within 1.1 pm and angles accurate to within 0.1° , even with frozen core approximations and without use of symmetries. The fact that both DFT and MCSCF, two very different theories, converged on a square pyramid as a local minimum energy structure raises the interesting possibility that this is an actual *meta*-stable conformer of $\text{Fe}(\text{CO})_5$.

The results of this work are consistent with the literature results previously cited. It is significant that the MCSCF results were achieved systematically without resorting to chemical information that would not

normally be available for novel molecular catalyst systems. It is equally significant that a minimal basis set, small active space MCSCF calculation found the qualitatively correct solution for an iron pentacarbonyl. Clearly, at this point, if this were a study of an uncharacterized catalytic intermediate instead of a test molecule, DFT would be the method of choice for further calculations; HF is not sufficiently accurate and the computational expense of MCSCF is not warranted. All three approaches (RHF, DFT and MCSCF) indicate the square pyramid as a minimum energy structure. DFT and MCSCF show it to be a local minimum that is higher in energy than the global minimum trigonal bipyramid structure. RHF shows the square pyramid as the only minimum energy structure. These findings suggest that the square pyramid geometry might be a *meta*-stable iron pentacarbonyl conformer.

Iron chlorides have been investigated using various quantum chemical formalisms as well. Some of the earlier work was done by Deeth et al. [22] who carried out DFT calculations on first row transition metal clusters, including $[\text{FeCl}_4]^-$. They compared the calculation results to polarized neutron diffraction data, and discovered that the magnitude of spin transfer from the transition metal center to the ligands was underestimated in the calculations. Later, Butcher et al. [23] studied the same iron cluster with photon energy photoelectron spectroscopy and DFT calculations. They found what they referred to as an inverted bonding scheme. The usual expectation for the transition metal orbital energies would place the non-bonding transition metal d -orbitals at the top, with the ligand orbitals below them. Their experiments showed that the higher energy orbitals contained substantial amounts of chlorine $3p$ character. Still, they noted that the cluster spin density was mostly localized around the iron atom.

Bach et al. [24] investigated single iron chlorides and their ions at QCISD(T) and MP2 levels of theory. FeCl_2^+ was not adequately described by QCISD because of contributions from non-ground state configurations; Brueckner doubles treatment was used for this species instead. Bond lengths changed little between MP2, QCISD, and DFT calculations, but there were significant differences among them in the values of calculated energies. Comparable bond lengths simply did not indicate comparable wavefunction accuracies. DFT with larger basis set performed better in

capturing correct bond dissociation energies than more expensive ab initio theory with smaller basis sets did.

Glukhovtsev et al. [25] investigated the performance of B3LYP functionals using effective core potential basis sets on iron containing compounds. They examined iron hydrides, oxides, species with hydrocarbon ligands, and halides. The geometries obtained were in generally good agreement with experimental data; more importantly, calculated energies compared reasonably with experimental data as well. However, these calculations all involved species with a single

iron atom; the authors were not confident that similar calculations would be as successful for multi-iron systems.

Choe et al. [26,27] investigated iron porphine with multi-reference perturbation theories, choosing their active space around iron-d-orbitals. The purpose of those studies was to elucidate the nature of the electronic ground state and other detailed electronic properties of the cluster. Dinuclear transition metal systems were investigated by Richter et al. [28,29]. They reported observing some anti-ferromagnetic coupling

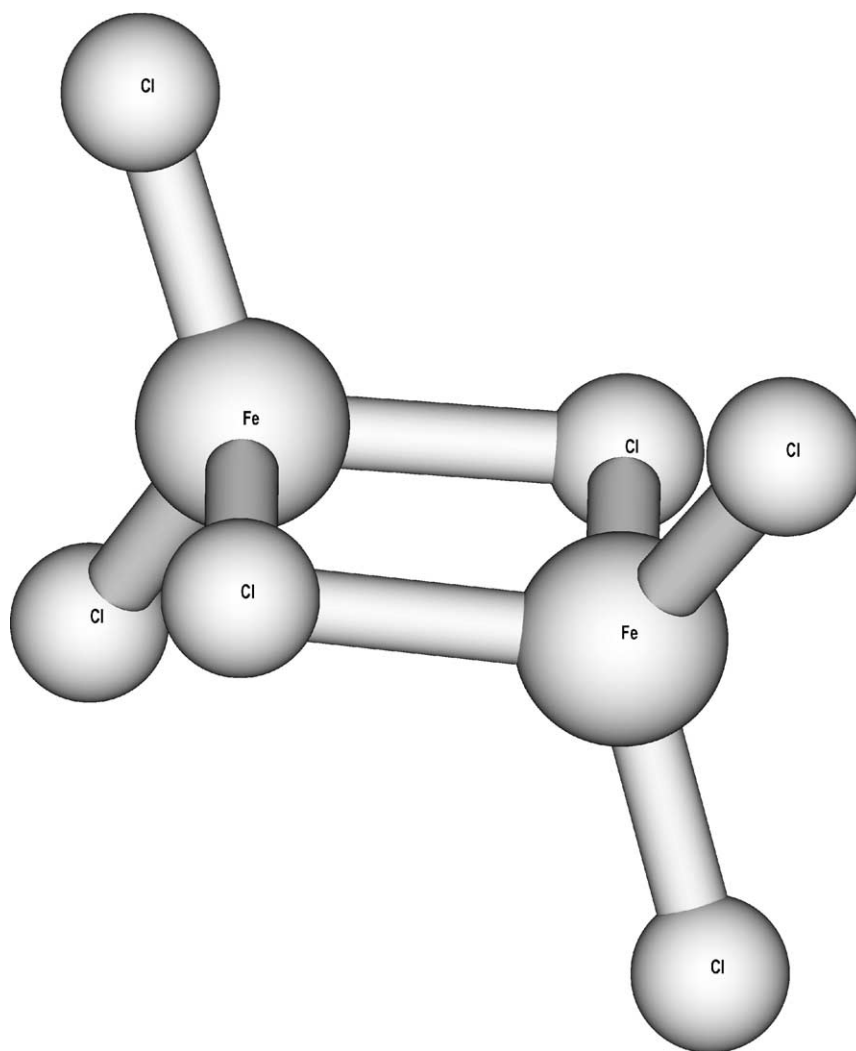


Fig. 8. Planar ring Fe_2Cl_6 minimum energy structure identified by HF, DFT and MCSCF calculations. It is the only minimum energy structure found by HF and DFT; MCSCF identified a puckered ring structure as being lower in energy.

between the transition metals in the well-characterized species they examined; the use of symmetry eliminated the possibility of serious geometric errors.

The present investigation of Fe_2Cl_6 again began with HF calculations. Different starting geometries were used, but HF geometry optimizations invariably converged to a planar ring structure like that shown in Fig. 8. DFT geometry optimizations also gave a planar final structure, irrespective of the starting geometry. In contrast, depending on the initial guess, MCSCF converged either to a planar structure or to a puckered ring structure like that shown in Fig. 9. The converged puckered MCSCF geometry was among the starting HF and DFT geometries, but in both of those cases, subsequent geometry optimization led to a final planar structure. The geometries and energies are summarized in Table 1, including two entries for the experimental geometry. The experiments were conducted at ca. 190 °C where molecular vibrations were significant [30]. A planar equilibrium structure could not be ruled out altogether because the pucker axis is also the axis of the lowest mode thermal vibration that would be expected from a molecule of this general structure. Analogous clusters such as Al_2Cl_6 are known

to vibrate about the axis formed by the two bridging chlorines. The experiments measured an “equilibrium structure,” which is not necessarily the same as the electronic ground state structure. Aside from definitely vibrating about the pucker axis, there also is the possibility of the molecule being in one of the lower excited state structures. Table 1 shows that the converged MCSCF puckered geometry was lower in energy than the corresponding planar geometry. This result, along with the more likely interpretation of the experimental results, indicates that the puckered geometry is probably the true ground state structure and the planar geometry is a local minimum energy structure.

The ab initio based results are similar (Table 1), with very good values for the angle formed by the terminal chlorines with the iron vertex, but with less satisfactory values for the angle formed by the bridging chlorines. The opposite is true for the DFT results; the terminal chlorine bond angles are too small, but the bridging chlorine angles are better. Still, none of the computed values tries to capture any vibration induced deviations, so perhaps, this level of agreement is the best that can be expected against a vibrating cluster. The DFT bond lengths are slightly more

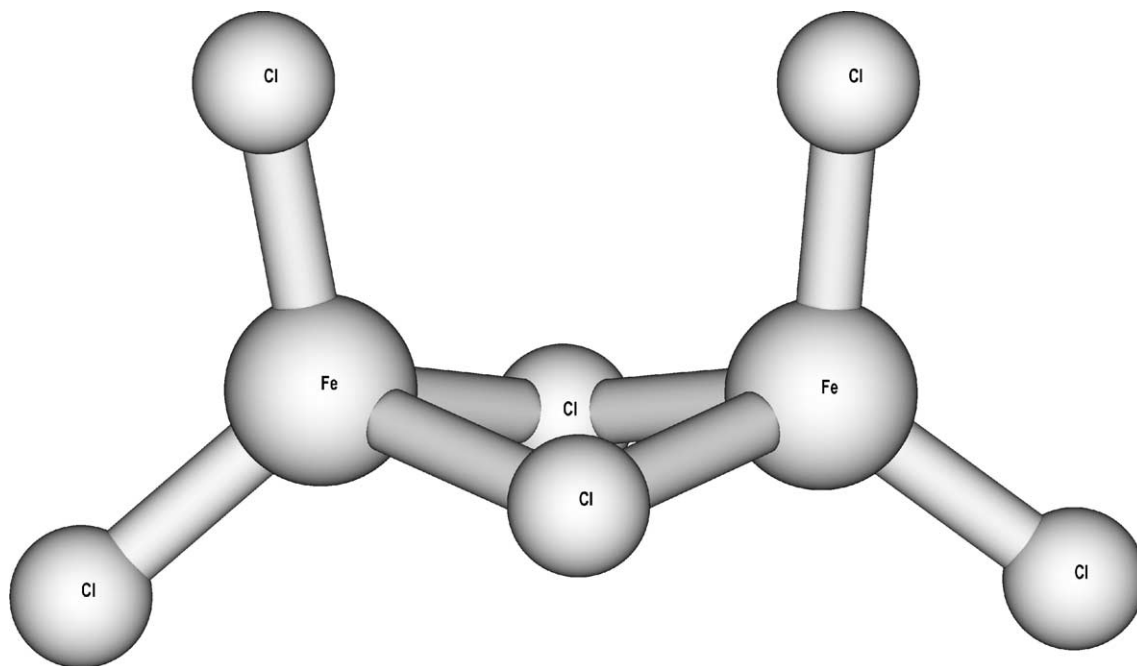


Fig. 9. Puckered ring Fe_2Cl_6 minimum energy structure identified by MCSCF calculations.

accurate than those obtained from the *ab initio* calculations, but this is probably because the DFT calculations used the most rigorous basis sets, including diffuse and polarization functions.

Again, the major result is that a relatively cheap MCSCF calculation, performed without the input of detailed chemical insight, found the qualitatively correct solutions for this model, finding correct symmetries despite a random orientation of atoms in the model. HF and DFT calculations did not. If this were a study of an uncharacterized catalytic site instead of a test molecule, it would seem that further study would have to be performed using MCSCF calculations. Alternatively, one might investigate whether a choice of exchange and correlation functionals other than B3LYP could be used to produce results comparable to the MCSCF results. More generally, the results from this work suggest that a preliminary MCSCF calculation may be useful when studying new, poorly characterized active sites containing iron or other transition metals. Such a calculation, when compared to DFT results, can show whether the less expensive methods are sufficiently accurate.

The size consistency issue of MCSCF remains unresolved. Fortunately, MCSCF calculations seem to produce the correct ordering of energies for similar clusters, so they may still be acceptable for preliminary examinations of similar species. Once the most promising candidate species have been identified, MCSCF calculations can always be extended to desired levels of quantitative accuracy. While anything short of an all-valence complete active space calculation would not be totally size consistent, the degree of inconsistency could probably be reduced to a level that permits meaningful quantitative comparisons among different species. Still, the size consistency issue needs further examination.

4. Conclusions

An approach for performing MCSCF calculations on species containing transition metals has been illustrated. It provides for generating an initial wavefunction by initially removing the complicating d-electrons and then gradually adding them back in. Once a good initial wavefunction is available, it uses a preliminary MCSCF calculation with a very large active space and

a very simple excitation scheme. The results from the preliminary MCSCF permit a systematic selection of the active space for the final calculations instead of relying on intuition or chemical insight. The approach was successfully applied to two model systems: iron pentacarbonyl and a ferric chloride dimer. The results from the calculations on iron pentacarbonyl raise the possibility of a *meta*-stable square pyramidal geometry with an energy slightly higher than the trigonal bipyramid structure. For ferric chloride, the MCSCF calculations predict a puckered ring structure as more favorable than a planar ring; ROHF and DFT fail to locate this puckered ring structure.

The results illustrate that MCSCF can be useful in molecular catalysis research. The iron pentacarbonyl calculations capture the correct overall shape and symmetries in spite of arbitrary axis choices. The ferric chloride calculations demonstrate a case where an MCSCF calculation has to be used to capture the qualitatively correct ground state geometry, and it also captures the correct symmetry. Neither of these calculations required expensive basis sets; in fact, the iron pentacarbonyl used minimal basis sets. Neither an intentionally random ordering of atoms nor the suppression of symmetries prevented successful geometry optimizations. A “manual” selection of active spaces was not necessary. Calculations like these can be used initially when studying a poorly defined or characterized catalytic species to determine whether a less expensive DFT calculation is adequate or whether the more expensive MCSCF approach is warranted.

Acknowledgements

This material is based upon work supported, in part, by the National Science Foundation under Award CTS-0099359. It would not have been possible without access to the resources of the Center for Computational Research at the University at Buffalo, SUNY. The insightful comments of Drs. Harry King, Jeff Tilson, and Dick Stanton are also most gratefully acknowledged.

References

- [1] J. Leglise, J.O. Petunchi, W.K. Hall, *J. Catal.* 86 (1984) 392.
- [2] C.M. Fu, V.N. Korchak, W.K. Hall, *J. Catal.* 68 (1981) 166.

- [3] H.Y. Chen, W.M.H. Sachtler, *Catal. Today* 42 (1998) 73.
- [4] H.Y. Chen, W.M.H. Sachtler, *Catal. Lett.* 50 (1998) 125.
- [5] C. Sang, C.R.F. Lund, *Catal. Lett.* 73 (2001) 73.
- [6] O. Hübner, V. Termath, A. Berning, J. Sauer, *Chem. Phys. Lett.* 294 (1998) 37.
- [7] A.V. Arbuznikov, M. Hendrickx, L.G. Vanquickenborne, *Chem. Phys. Lett.* 310 (1999) 515.
- [8] M.W. Schmidt, K.K. Baldrige, J.A. Boatz, S.T. Elbert, M.S. Gordon, J.J. Jensen, S. Koseki, N. Matsunaga, K.A. Nguyen, S. Su, T.L. Windus, M. Dupuis, J.A. Montgomery, *J. Comp. Chem.* 14 (1993) 1347.
- [9] G. Schaftenaar, J.H. Noordik, *J. Comput. Aided Mol. Des.* 14 (2000) 123.
- [10] A.J.H. Wachtters, *J. Chem. Phys.* 52 (1970) 1033.
- [11] Jaguar, 3.5, 4.0 ed.; Schrodinger Inc., Portland, OR, 1998.
- [12] H.P. Lüthi, P.E.M. Siegbahn, J. Almlöf, *J. Phys. Chem.* 89 (1985) 2156.
- [13] S. Yamamoto, J. Teraoka, H. Kashiwagi, *J. Chem. Phys.* 88 (1988) 303.
- [14] S. Yamamoto, H. Kashiwagi, *Chem. Phys. Lett.* 161 (1989) 85.
- [15] S. Yamamoto, H. Kashiwagi, *Chem. Phys. Lett.* 205 (1993) 306.
- [16] A. Ghosh, J. Almlöf, J.L. Que, *J. Phys. Chem.* 98 (1994) 5576.
- [17] L.A. Barnes, B. Liu, R. Lindh, *J. Chem. Phys.* 98 (1993) 3978.
- [18] L.A. Barnes, M. Rosi, C.W.J. Bauschlicher, *J. Chem. Phys.* 94 (1991) 2031.
- [19] A. Marquez, C. Daniel, J.F. Sanz, *J. Phys. Chem.* 96 (1992) 121.
- [20] O. Rubner, V. Engel, M.R. Hachey, C. Daniel, *Chem. Phys. Lett.* 302 (1999) 489.
- [21] H. Jacobesn, T.J. Ziegler, *Am. Chem. Soc.* 118 (1996) 4631.
- [22] R.J. Deeth, B.N. Figgis, M.I. Ogden, *Chem. Phys.* 121 (1987) 115.
- [23] K.D. Butcher, S.V. Didziulis, B. Briat, E.I. Solomon, *J. Am. Chem. Soc.* 112 (1990) 2231.
- [24] R.D. Bach, D.S. Shobe, H.B. Schlegel, C.J. Nagel, *J. Phys. Chem.* 100 (1996) 8770.
- [25] M.N. Glukhovtsev, R.D. Bach, C.J. Nagel, *J. Phys. Chem. A* 101 (1997) 316.
- [26] Y.K. Choe, T. Hashimoto, H. Nakano, K. Hirao, *Chem. Phys. Lett.* 295 (1998) 380.
- [27] Y.K. Choe, T. Nakajima, K. Hirao, R. Lindh, *J. Chem. Phys.* 111 (1999) 3837.
- [28] U. Richter, J. Heck, J. Reinhold, *Inorg. Chem.* 38 (1999) 77.
- [29] U. Richter, J. Reinhold, J. Heck, *Inorg. Chem.* 39 (2000) 658.
- [30] M. Hargittai, J. Tremmel, I. Hargittai, *J.C.S. Dalton* 1 (1980) 87.
- [31] D. Braga, F. Grepioni, A.G. Orpen, *Organometallics* 12 (1993) 1481.