

Theoretical study of the electronic ground state of iron(II) porphine

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Abstract

Ten low-lying electronic states of Fe(II)-porphine, the $^5A_{1g}$, 5E_g , $^5B_{2g}$, $^3A_{2g}$, $^3B_{2g}$, $^3E_g(A)$, $^3E_g(B)$, $^1A_{1g}$, $^1B_{2g}$ and 1E_g states, are studied with multireference Møller–Plesset perturbation theory with complete active space self-consistent field (CASSCF) reference functions. Triplet and singlet states are significantly multiconfigurational in character. The ten low-lying states are computed to be within a 2 eV span and the $^5A_{1g}$ state is predicted to be the lowest. At the CASSCF level, all the quintet states are lower in energy than the triplets. This tendency is reversed, except for the $^5A_{1g}$ state, after perturbation theory is applied. Among controversial candidates for the triplet ground state, the 3E_g state is computed to be more stable, by 0.18 ~ 0.23 eV, than the $^3A_{2g}$ and $^3B_{2g}$ states. © 1998 Elsevier Science B.V. All rights reserved.

1. Introduction

For a long period, iron porphine has attracted much interest from chemists, since it participates in very important biological processes such as oxygen transport and electron transfer processes. In spite of its significance, there still remain problems to be solved. In particular, the spatial symmetry of the ground state configuration has been questioned by both experimental and theoretical chemists [1–9]. Possible ground state configurations are $^5A_{1g}$, 5E_g , $^5B_{2g}$, $^3A_{2g}$, $^3B_{2g}$, $^3E_g(A)$, $^3E_g(B)$, $^1A_{1g}$, $^1B_{2g}$ and 1E_g .

NMR results by Goff et al. show that the $^3A_{2g}$ state is the spatial symmetry of the ground state

configuration owing to the large π contact shifts [8]. However, resonance Raman results on Fe(II)-octaethylporphine by Kitagawa et al. support the 3E_g ground state, since its spectrum displayed the characteristic features of iron porphines with three d_π electrons [9]. The ground state is also assigned to be the 3E_g state by Obara et al. based on their interpretation of Mössbauer spectra aided by ab initio calculations [1]. Ab initio configuration interaction (CI) calculations by Rawlings et al. show that the 5E_g state is the lowest in energy within the CI space employed in their calculations [3]. Large-scale CI calculations of Rohmer suggest that the $^3A_{2g}$ state is lower than the 3E_g state by 0.27 eV [4]. $X\alpha$ calculations by Sountum et al. prefer the $^3A_{2g}$ state to the 3E_g state [2]. Based on their density functional studies, Delly [6] and Matsuzawa et al. [7] predict that the 3E_g state is the ground state. As seen above, a

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Table 1
Optimized geometry parameters for Fe(II)-porphine

	$^5A_{1g}$	5E_g	$^5B_{2g}$	$^3A_{2g}$	3E_g	$^1A_{1g}$	$^1B_{2g}$	1E_g
Bond distance (Å)								
Fe–N2	2.074	2.076	2.073	2.033	2.034	2.033	2.033	2.033
N2–C7	1.364	1.363	1.363	1.366	1.366	1.366	1.366	1.366
C7–C15	1.444	1.445	1.445	1.440	1.440	1.441	1.440	1.442
C14–C15	1.354	1.354	1.354	1.352	1.352	1.352	1.352	1.352
C7–C23	1.390	1.392	1.389	1.382	1.382	1.382	1.382	1.382
C15–H27	1.075	1.076	1.076	1.076	1.076	1.075	1.076	1.075
C23–H35	1.082	1.082	1.083	1.082	1.082	1.082	1.082	1.082
Bond angle (°)								
C6–N2–C7	108.6	108.6	108.6	107.3	107.3	107.3	107.3	107.3
N2–C7–C23	125.5	125.5	125.6	125.6	125.6	125.6	125.6	125.6
C8–C23–C7	127.5	127.6	127.5	126.2	126.2	126.2	126.2	126.2
N2–C7–C15	108.4	108.4	108.4	109.2	109.2	109.3	109.2	109.2
C7–C15–C14	107.3	107.3	107.3	107.1	107.1	107.1	107.1	107.1

The same geometry was used for $^3A_{2g}$ and $^3B_{2g}$.

conclusion regarding the ground state configuration has not yet been reached and this topic has been a challenge to theoretical chemists.

The recent developments of ab initio quantum chemistry have made it possible to study relatively large molecules with quantitative accuracy. Particu-

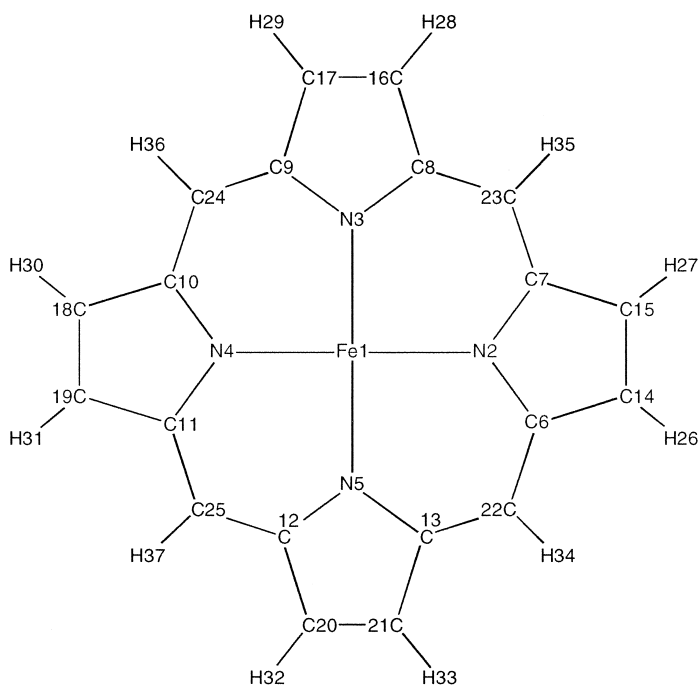


Fig. 1. Molecular geometry for Fe(II)-porphine.

larly, multireference Møller–Plesset perturbation theory (MRMP) [10–13] has proved useful in treating various chemical problems [14]. In this Letter, we will present MRMP calculations on the electronic ground state of four-coordinate Fe(II)-porphine. The purpose of this Letter is to contribute to the elucidation of the ground state configuration of Fe(II)-porphine and to apply MRMP to a large open-shell molecule to confirm its utility. It should be emphasized that this is the first attempt to approach the solution of this problem using the recently developed theory of ab initio quantum chemistry and it will serve as a guide to the solution of the problem. No other calculations on this molecule have been made at the level of theory employed in this study, which takes into account both dynamic and non-dynamic correlation. The limitations of the method and the suggestion for further work will be given.

2. Computational details

The calculations were performed for each of the possible ground state configurations of Fe(II)-porphine. The ground state geometries were optimized using the CASSCF level of theory for each configuration. In geometry optimization, we considered the six d electrons of Fe to be distributed among the five d orbitals which constitute the active orbitals. The molecule has D_{4h} symmetry and is placed in the xy -plane.

The basis sets used were derived from Dunning's cc-pVDZ sets [15]. We used (9s4p)/[2s2p] for carbon and nitrogen and (4s)/[2s] for hydrogen, respectively. For iron, the (14s8p5d) set was contracted to [5s3p2d] [16].

We calculated the energy of the molecule by CASSCF calculations with larger active space using the optimized geometries. The active space employed was as follows: the active orbitals are the six π and π^* orbitals of the porphine ring plus the five d orbitals of Fe and the active electrons are the four π electrons of the porphine ring and the six d electrons of iron. Thus, ten electrons are distributed

among eleven active orbitals. Then, we applied MRMP to each state obtained with CASSCF. The influence of the σ electrons and the remaining π electrons is included in a perturbation treatment.

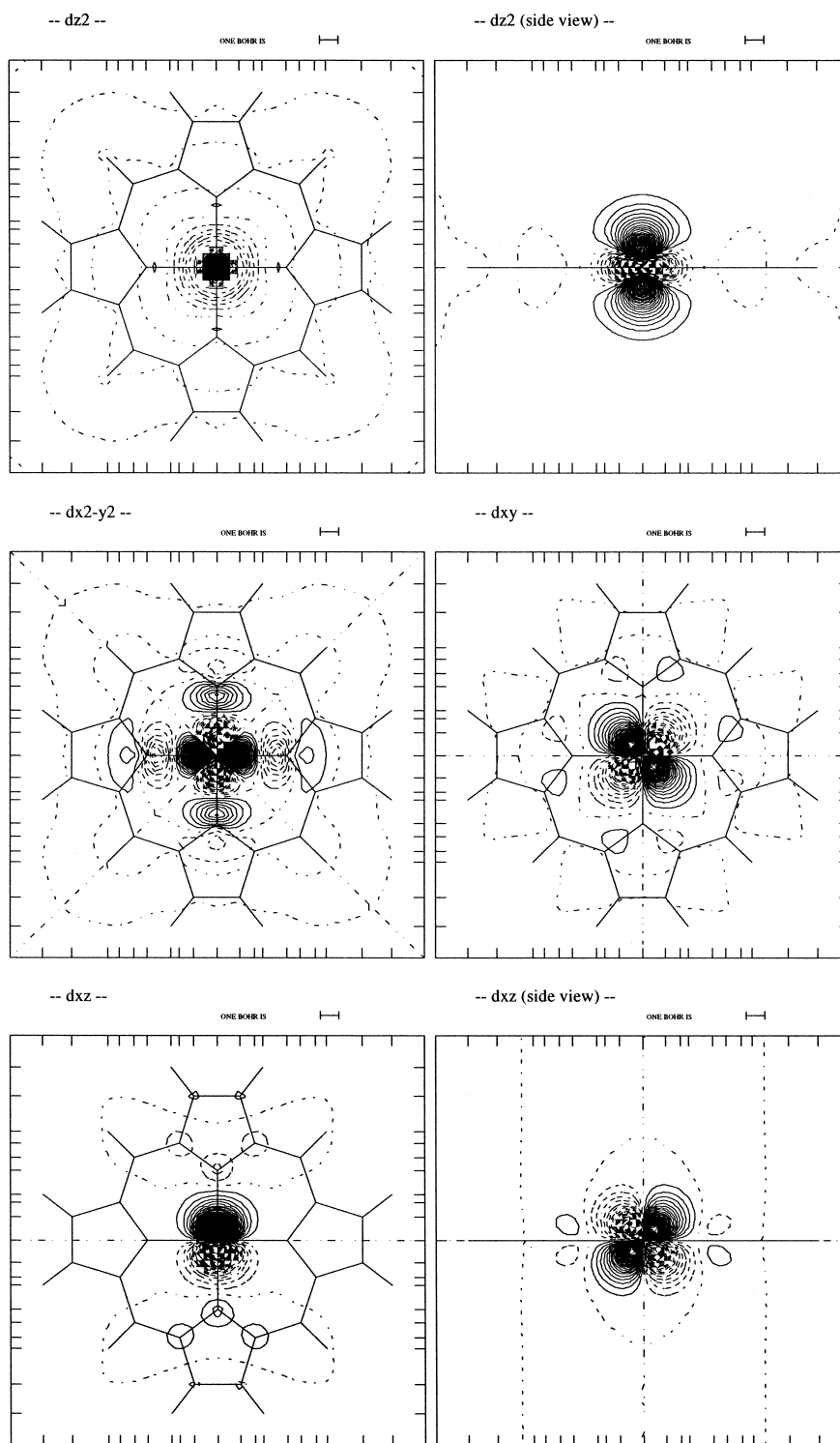
3. Results and discussions

3.1. Geometry

Table 1 shows optimized geometries of each state. The molecular geometry and numbering of atoms are seen in Fig. 1. As seen in the table, within the same spin multiplicity the variations of the geometries are not so great. Of importance in geometry is the Fe–N bond length since it is related to the spin multiplicity of the molecule [2,5]. Comparison with the experimental geometry of FeTPP (tetraphenylporphine) shows that our results (2.033–2.076 Å) for the Fe–N bond length are somewhat longer than the experimental value of 1.97 Å [17]. The results obtained by density functional theory are shorter than the experimental observation ~ 0.01 Å [6,7].

Sontum et al. have mentioned (based on their $X\alpha$ results) that the longer Fe–N distance prefers a high-spin structure to an intermediate one [2]. Our results are consistent with this. A major reason for the elongation of the Fe–N bond arises from the nature of the molecular orbitals, including, the $d_{x^2-y^2}$ orbital, of iron. The d orbitals of iron obtained by CASSCF calculations are shown in Fig. 2. It is shown that the $d_{x^2-y^2}$ orbital has a strong antibonding character originating from a negative overlap with neighboring nitrogen thus making the energy of the molecular orbital higher. For singlet and triplet states, the $d_{x^2-y^2}$ orbital remains unoccupied. On the contrary, when an electron occupies the $d_{x^2-y^2}$ orbital the Fe–N bond is elongated. The Fe–N bond lengths in the quintets are computed to be longer by 0.04 Å than those of the triplet and singlet states. Previous ab initio studies have not taken this effect into consideration. The Fe–N bond length employed

Fig. 2. Plots of CASSCF natural orbital of the d orbitals of iron. The d_{yz} orbital was not plotted since d_{xy} and d_{yz} are degenerate within D_{4h} symmetry.



in the previously reported ab initio calculations were between 1.97 and 2.01 Å. At shorter bond lengths, the triplet is favored; however, using longer bond lengths favours the quintet state. Therefore, the calculation of energy based on the same fixed geometry for both spin states is not adequate for this system.

3.2. Energetics

Table 2 shows energies of the possible states relative to the ${}^3E_g(A)$ state. Although previous ab initio calculations are limited, there are some semiempirical and density functional calculations of Fe(II)-porphine. The present results are compared to the previous calculations in Table 2. The CASSCF configurations for the low-lying electronic states are given in Table 3.

At the CASSCF level, the ten low-lying states are calculated to be in a narrow energy span. The relative order is

$${}^5A_{1g} < {}^5E_g < {}^5B_{2g} < {}^3A_{2g} < {}^3E_g(A) < {}^3B_{2g} < {}^3E_g(B) \\ < {}^1A_{1g} < {}^1E_g < {}^1B_{2g}.$$

The quintet states are computed to be the lowest, and triplet states are the next lowest, at the CASSCF level. The singlet states are calculated to be less stable than the high-spin states. However, the intro-

duction of the dynamical correlation changes the picture dramatically. MRMP predicts the relative order

$${}^5A_{1g} < {}^5E_g(A) < {}^1A_{1g} < {}^3B_{2g} < {}^3A_{2g} < {}^5E_g < {}^3E_g(B) \\ < {}^5B_{2g} < {}^1A_{1g} < {}^1E_g.$$

All states are again predicted to exist within a narrow energy span of 2 eV. These changes are shown in Fig. 3. CASSCF overestimates the stability of high-spin states and MRMP corrects the deficiency by taking the dynamical correlation into account. A similar tendency is also found in the previous SCF and CI calculations. The lower level of theory tends to favor the high-spin states. Rawlings et al. did the full CIs in the nine orbitals which consist of five 3d MOs on iron and two highest occupied π and two lowest unoccupied π^* orbitals and then calculated single excitations from this space into five d^* MOs and into s and p Rydbergs [3]. Their results show that the quintets are more stable than triplets. They also predicted that large CI calculations, or the application of perturbation sums over all of the virtual orbitals, would decrease the energy of the triplets and increase the energy of the quintets. The level of their calculations is in between the present CASSCF and MRMP results. Our results agree with the prediction given by them as seen in Table 2. The results of Rawlings et al. are different from the present

Table 2
CASSCF and MRMP energies (eV) for low-lying states of Fe(II)-porphine relative to the ${}^3E_g(A)$ state^a

State	CASSCF ^b	MRMP ^b	ZINDO ^c	Ab initio			DFT ^f	DFT ^g
				SCF ^d	CI ^d	CI ^e		
${}^5A_{1g}$	-1.347	-0.369	0.28	-1.40	-0.10		1.44	1.52
5E_g	-0.878	0.481	0.39	-1.19	-0.83		1.29	
${}^5B_{2g}$	-0.343	0.652	0.63	-1.05	0.09		1.74	1.76
${}^3A_{2g}$	-0.003	0.229	-0.03	-0.29	0.47	-0.27	0.25	0.19
${}^3B_{2g}$	0.518	0.177	0.39	0.51	0.20		0.53	0.58
${}^3E_g(A)$	0.000	0.000	0.00	0.00	0.00	0.00	0.00	0.00
${}^3E_g(B)$	1.115	0.632	1.03	1.41	1.12		0.88	
${}^1A_{1g}$	1.263	0.171	0.98	1.36	1.06		1.20	1.24
${}^1B_{2g}$	1.568	1.270	1.76	1.58	1.6			
1E_g	1.350	1.508	0.93		1.33			

^aCASSCF and MRMP energies of the ${}^3E_g(A)$ state are -2243.79332 and -2245.48704 hartree, respectively.

^bThis work. ^cFrom Ref. [5]. ^dFrom Ref. [3]. ^eFrom Ref. [4]. ^fFrom Ref. [6]. ^gFrom Ref. [7].

Table 3
Main configurations in CASSCF wavefunctions

State	CI coefficient	Dominant configurations										
		d_{z^2}	$d_{x^2-y^2}$	d_{xy}	d_{yz}	d_{xz}	$a_{2u\pi}$	$a_{2u\pi}^*$	$e_{gx\pi}^*$	$e_{gy\pi}^*$	$a_{1u\pi}$	$a_{1u\pi}^*$
$^5A_{1g}$	0.9610	2	1	1	1	1	2	0	0	0	2	0
	0.1038	2	1	1	1	1	1	0	1	1	1	0
5E_g	0.9901	1	1	1	2	1	2	0	0	0	2	0
$^5B_{2g}$	0.9612	1	1	2	1	1	2	0	0	0	2	0
	0.1039	1	1	2	1	1	1	0	1	1	1	0
$^3A_{2g}$	0.9414	2	0	2	1	1	2	0	0	0	2	0
$^3B_{2g}$	0.8961	1	0	1	2	2	2	0	0	0	2	0
	-0.2232	1	1	2	1	1	2	0	0	0	2	0
	0.1572	1	1	2	1	1	2	0	0	0	2	0
$^3E_g(A)$	0.8789	1	0	2	1	2	2	0	0	0	2	0
	0.3400	2	0	1	2	1	2	0	0	0	2	0
$^3E_g(B)$	0.6680	2	0	1	2	1	2	0	0	0	2	0
	0.3957	1	1	1	2	1	2	0	0	0	2	0
	0.3231	2	1	2	1	0	2	0	0	0	2	0
	-0.2337	1	0	2	1	2	2	0	0	0	2	0
	-0.2775	1	1	1	2	1	2	0	0	0	2	0
	-0.1937	1	1	1	2	1	2	0	0	0	2	0
	-0.1435	2	2	1	0	1	2	0	0	0	2	0
	-0.1335	2	1	0	1	2	2	0	0	0	2	0
$^1A_{1g}$	0.8877	0	0	2	2	2	2	0	0	0	2	0
	-0.2124	2	0	2	0	2	2	0	0	0	2	0
	-0.2124	2	0	2	2	0	2	0	0	0	2	0
	0.1452	0	0	2	2	2	1	0	1	1	1	0
	-0.1298	2	0	0	2	2	2	0	0	0	2	0
$^1B_{2g}$	0.8863	2	0	2	1	1	2	0	0	0	2	0
	-0.1856	2	1	1	0	2	2	0	0	0	2	0
	0.1856	2	1	1	2	0	2	0	0	0	2	0
	-0.1542	1	0	1	2	2	2	0	0	0	2	0
1E_g	0.9130	1	0	2	1	2	2	0	0	0	2	0
	0.1946	0	1	2	1	2	2	0	0	0	2	0
	0.1341	2	0	1	2	1	2	0	0	0	2	0
	0.1295	1	0	2	1	2	1	0	1	1	1	0

study on account of the difference in the size of CI space and the electron correlation method employed.

Table 3 shows that the quintet states are described well by a single configuration but triplet and singlet states, especially the $^3B_{2g}$, $^3E_g(A)$, $^3E_g(B)$ and $^1A_{1g}$ states, are significantly multiconfigurational in character. It is noted that the coefficient of each main configuration is < 0.9 and there is a strong admixture of the doubly excited configurations with the different 3d electron configuration to the wavefunc-

tion. The $^3E_g(B)$ state is represented by a mixture of three configurations and there is no dominant configuration. The quintet and singlet state wavefunctions also include doubly excited configurations among the porphine ring π space, although there is no such contribution in the triplet states.

The single configurational high-spin states and the multiconfigurational intermediate- and low-spin states, exhibit different behavior as far as the dynamical electron correlation is concerned. Dynamical

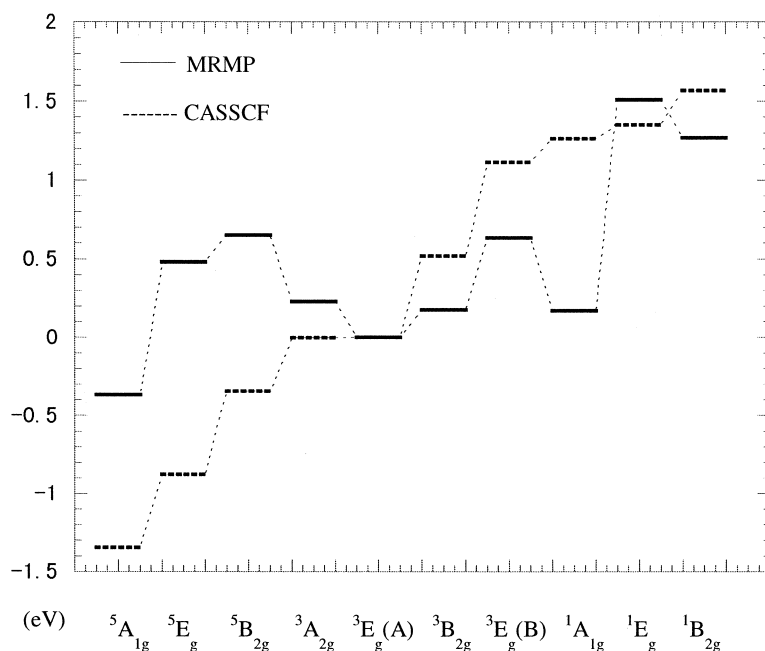


Fig. 3. Relative energies of CASSCF and MRMP of Fe(II)-porphine for each state.

correlation favors the multiconfigurational states relative to the single configurational states. Thus, MRMP stabilizes the multiconfigurational $^3B_{2g}$, $^3E_g(A)$, $^3E_g(B)$ and $^1A_{1g}$ states more than the other single configurational states. The interval between the $^5A_{1g}$ state and the $^3E_g(A)$ state decreases significantly in going from CASSCF (1.35 eV) to MRMP (0.37 eV), although the single configurational $^5A_{1g}$ state remains the lowest even at the level of MRMP. The $^3B_{2g}$ and $^1A_{1g}$ states are also markedly stabilized and become very close to the $^3E_g(A)$ state.

Rohmer estimated how much correlation energy was recovered for this molecule by increasing the number of electrons correlated [4]. She first performed CI calculations with 56 active orbitals and expanded CI space by adding 13π orbitals of the porphine ring. Her calculations show that when only the d electrons of the iron were correlated the energy lowering is larger for the 3E_g state than for the $^3A_{2g}$ state. On the other hand, when the CI space was extended to include 26π electrons of the porphyrin ring, it was found that such an expansion gives almost the same effect for both $^3A_{2g}$ and 3E_g states with a similar order of lowering. MRMP predicts

that more correlation energy is recovered in the multiconfigurational 3E_g state than in the $^3A_{2g}$ state. The multiconfigurational character of the 3E_g state is mainly due to the configuration mixing with the low-lying $^3E_g(B)$ state. This effect of configuration mixing is calculated to decrease the energy of the 3E_g state with respect to the $^3A_{2g}$ state by Obara et al. [1] but later, as mentioned above, found to be of little importance by Rohmer. The difference between Rohmer's results and those of the present study arises from the character of the electron correlation considered. Her calculations show that within the single determinant based non-dynamical electron correlation treatment, the effect is similar for both states.

MRMP strongly suggests that the further treatment of correlation that is of dynamical character should contribute to the relative energy of each state, which leads to an opposite conclusion to that of Rohmer's. To compute the energy of this molecule with given spatial and spin symmetry correctly, therefore, it is pointed out that the effect of both dynamical and non-dynamical correlation should be explicitly included in the method of calculation.

Moreover, a multiconfigurational character is found to be of importance for the computation of this molecule since the single-determinant based method inevitably leads to an incorrect description of the state. These results give us an insight that the further consideration of electron correlation would lower the energy of triplet states relative to other possible ground state configurations.

For further work, some points can be suggested from this study. The molecular orbital plots in Fig. 2 show that except for the $d_{x^2-y^2}$ orbital, the d orbitals of iron which were included in the active space do not have a large overlap with neighboring orbitals. The $d_{x^2-y^2}$ orbital has an antibonding interaction with neighboring nitrogen. This orbital is important in determining the spin multiplicity of this molecule because it is occupied only in case of the quintets. Thus, it may be concluded that an extension of basis sets, especially for iron and nitrogen, is desirable to describe the energy of this molecule. As mentioned above, the states that have multiconfigurational character are found to be very sensitive to the effect of electron correlation. Therefore, the further consideration of electron correlation, especially the expansion of the active space of reference CASSCF functions, may lower the energy of these states rather than the other candidates for the ground state.

4. Conclusions

Ten electronic states of Fe(II)-porphine were studied using MRMP. Five ($^3B_{2g}$, $^3E_g(A)$, $^3E_g(B)$, $^1A_{1g}$, $^1B_{2g}$) states are significantly multiconfigurational in character, which causes the ordering of the states to be difficult due to the narrow energy span. MRMP predicts the $^5A_{1g}$ state to be lowest. However, this conclusion does not necessarily agree with experimental observations. It is found that the geometry has such a significant effect on the energy of this molecule that one should use the optimal geometry for each spin multiplicity. The geometry optimizations prove that the longer Fe–N bond favors high spin, rather than an intermediate one, because of the nature of the $d_{x^2-y^2}$ orbital of iron. At the CASSCF level, the quintet states are found to be more stable than the triplets. The application of MRMP to each state lowers the energy of triplets with respect to 5E_g

and $^5B_{2g}$ states. Also, we found that the energy gap between the $^5A_{1g}$ and 3E_g state decreases by taking the dynamical correlation into account. Hence, the order of energy is reversed at the MRMP level. It is found that the dynamic electron correlation lowers the energy of triplets more than the quintets. Further, the dynamical correlation lowers the energy of the 3E_g states rather than $^3A_{2g}$ state. This suggests the possibility that one of the triplet states could be the ground state configuration if more electrons were correlated.

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