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Electronic States of Dioxygen Heme Complex Revealed from *ab Initio* LCAO-SCF-MO Calculations

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Ab initio LCAO-SCF-MO calculations of a model oxyheme were carried out on several singlet, triplet and quintet states arising from the three types of configurations, $(d_\varepsilon)^6(\pi_g^a)^2$, $(d_\varepsilon)^5(d_\gamma)^1(\pi_g^a)^1(\pi_g^b)^1$, and $(d_\varepsilon)^5(\pi_g^a)^2(\pi_g^b)^1$. The lowest states in the SCF energy are of the configuration $(d_\varepsilon)^5(\pi_g^a)^2(\pi_g^b)^1$ whose electronic structures can be also expressed as Fe(III)–O_2^- from the results of Mulliken's population analysis. Calculated Mössbauer parameters of those states are in good agreement with experiments for oxyhemoglobin, oxymyoglobin and model oxyheme, while those of the closed-shell singlet state $(d_\varepsilon)^6(\pi_g^a)^2$ are inconsistent with experiments. The Fe–O_1 overlap populations indicate a bonding nature for the former states and a non-bonding nature for the latter state. These results all predict singlet states of Fe(III)–O_2^- structure as the main configuration of the ground state in the model oxyheme.

The nature of the iron-oxygen bond in oxyhemoglobin and oxymyoglobin is a controversial problem. Although X-ray data from a model oxyheme[1] and oxymyoglobin[2] support the bent Fe–O_1–O_2 geometry proposed by Pauling,[3] questions concerned with the details of the bondings and the charge on the oxygen molecule have not yet been resolved.

Mössbauer resonance of the proteins[4–6] and of the model compound[7] has been used to probe the electron distribution around the iron nucleus. Electronic transitions spectra,[8,9] magnetic circular dichroism spectra,[9,10] infrared stretching frequencies,[11–14] resonance Raman frequencies,[15,16] magnetic susceptibility,[17–22] and the Fe $K\alpha$ fluorescence emission spectrum of oxyhemoglobin[23] have been measured in order to elucidate the bonding of dioxygen to iron porphyrins.

The large quadrupole splitting observed in Mössbauer resonance of the oxyhemoglobin[5,6] and of the model oxyheme compound,[7] would imply the presence of large asymmetric 3d electron distribution caused by covalent bondings if the oxyhemoglobin were to be considered as low-spin iron(II). However the observed negative electric field gradient would be compatible with the loss of electron charge from a dπ orbital, which may imply an Fe(III)–O_2^- structure.

The oxygen-oxygen stretching frequencies observed in myoglobin (1103 cm^{-1}),[11] in hemoglobin (1107 cm^{-1}),[12] and in the model compounds (1160 cm^{-1})[13] were cited as evidence for the Fe(III)–O_2^- structure, since they fall in the range found for superoxide complexes (KO_2, 1100—1150 cm^{-1}), while the stretching frequencies for the O_2 molecule are 1556 cm^{-1} for the $^3\Sigma_g^-$ state and 1484 cm^{-1} for the $^1\Delta_g$ state. However the force constant of the O–O bond in ozone (6.16 mdyn/Å) displayed a similar value to that for the O_2^- complex (5.7—6.2 mdyn/Å). This suggests that a neutral O_2 unit in heme complexes can have the observed frequencies mentioned above (1 mdyn/Å$=1\times10^{-7}$ N nm^{-1}).

Thus no definite conclusion can be drawn from experimental measurements. Many theoretical calculations[24–35] have been made to try to resolve these uncertainties and to account for the observed properties of oxyhemoglobin.

Recent semi-empirical INDO-SCF-CI calculations on a model oxyheme complex were reported to yield a singlet diamagnetic ground state with a very low-lying paramagnetic triplet state.[31] The diamagnetic ground state has considerable Fe(III)(d^5)–O_2^- character due to extensive charge-transfer but is not described by a single open-shell configuration of the Fe(III)(d^5)–O_2^- type. The calculations gave a quadrupole splitting and an electric field gradient in agreement with experiments, using delicate sets of semi-empirical parameters.

Ab initio LCAO-SCF-MO calculations for the model oxyheme were made by Dedieu *et al.*[33–35] Both minimal and valence-double basis set calculations yielded the lowest energy for a triplet state $^3A'$ with the formal configuration $(d_{x^2-y^2})^2(d_{xz})^2(d_{yz})^1(\pi_g^a)^2(\pi_g^b)^1$. However they assigned the ground state to the closed-shell state ($^1A'$), $(d_{x^2-y^2})^2(d_{xz})^2(d_{yz})^2(\pi_g^a)^2$, which lies at 0.036 a.u. (in the minimal basis) and 0.051 a.u. (in the valence-double basis set calculation) higher than the triplet state, since they estimated the correlation energy to be larger than 0.051 a.u. (1 a.u.$=4.35968\times10^{-18}$ J). This ground state wavefunction could not reproduce experimental Mössbauer parameters.[27,28,34] These calculations of Dedieu *et al.*[33,34] employed a split basis for the iron 3d orbitals consisting of optimized atomic 3d orbitals and additional Gaussian functions with a small exponent of 0.20. In our previous *ab initio* LCAO-SCF-MO calculations on cobalt porphine with a triple zeta 3d set,[36] the Gaussian 3d functions with an exponent of 0.18 were found to be negligible, while those with an exponent of 0.555999 were found to be critical in the description of the electronic structures of high oxidation states (see Discussion). Similarly in the present study we have found that Dediue's description of 3d orbitals is not flexible enough accurately to compare energies between Fe(III)- and Fe(II)-complexes.

In the present investigation we have examined *ab initio* LCAO-SCF-MO calculations using a basis set different from Dedieu's sets with a hope to predict correct energy levels and Mössbauer parameters. In the following sections we give details of the calculation methods, then present the results, and discuss the total energies, Mössbauer parameters, charge distributions, and bonding natures for the oxyheme model.

Method

The geometry of the iron-porphine core, with the iron atom in the assumed porphine plane, was taken as the experimental geometry of the ($\alpha,\beta,\gamma,\delta$-tetraphenylporphinato)iron(II)(py)(CO)[37] (somewhat idealized) and is shown in Fig. 1a. For the Fe–O_1–O_2 moiety we have used an Fe–O_1 bond length of 1.75 Å, and an O_1–O_2 bond length of 1.24 Å and a Fe–O_1–O_2 angle of 136° corresponding to the experimental values for the dioxygen complex of the picket fence porphyrin.[7] We have used the experimental geometries of the ammonia ligand with an Fe–N bond length of 2.12 Å (Fig. 1b).[38] Our choice of axis is shown in Fig. 1b with the porphine plane being the xy plane. The four nitrogen atoms of the pyrrole rings are along the bisector of the axes x and y. The Fe–O_1 axis is the z axis and the O_1–O_2 axis projects along the axis x. The model system is assumed to have C_s symmetry.

Table 1(a). Orbital exponents (α) and contraction coefficients of the contracted gaussian type orbitals (CGTO's) for Fe

α	Contraction coefficients of CGTO's			
	1s	2s	3s	4s
63509.8	0.00169			
9344.59	0.01320			
2156.66	0.06284			
627.32	0.21100			
208.38	0.44009			
74.8588	0.38283			
19.2876		0.41810		
8.09403		0.67946		
2.14813			0.55185	
0.868997			0.68840	
0.260000				1.00000
α	2p	3p	4p	
424.039	0.02472			
98.9427	0.16155			
30.8593	0.45455			
10.7975	0.48537			
2.91785		0.53686		
0.924889		0.59877		
0.280000			1.00000	
α	$3d_1$	$3d_2$		
23.2006	0.06540			
6.13066	0.28749			
1.84927	0.51785			
0.505755		1.00000		

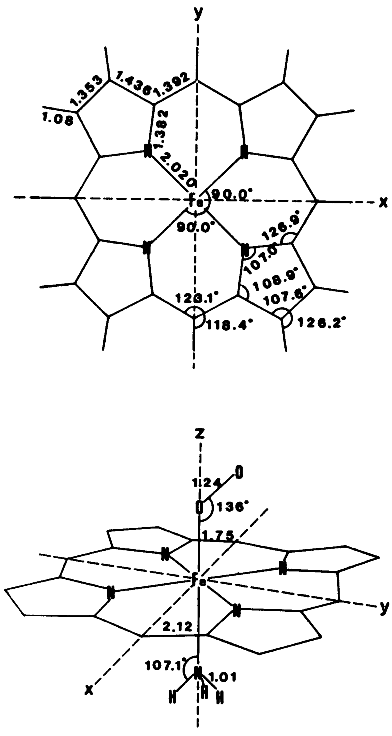

Fig. 1(a). Assumed geometry of the iron-porphine core for the oxyheme model and the choice of axes. Bond lengths are given in angstroms.
(b). The relative orientation and bond lengths (in angstroms) of the dioxygen and ammonia molecules in the oxyheme model.

The *ab initio* LCAO-SCF-MO calculations including all electrons have been carried out on the oxyheme model described above with a primitive Gaussian basis set (11s, 7p, 4d/7s, 3p/3s)[39,40] contracted to [4s, 3p, 2d/2s, 1p/1s] which is a minimal set except for the 3d functions with a split basis. The basis sets are shown in Table 1. For H, the (3s) set was contracted to the minimal set. The (7s, 3p) set was contracted to the minimal bases for C, O, and N. The (11s, 7p, 4d) basis set for the Fe atom is constructed from a (12s, 6p, 4d) basis optimized for Fe,[39] where two diffuse s functions were replaced by one s function of exponent 0.26; a set of p functions with an exponent of 0.28 was incremented. A comparison between ours and Dedieu's 3d orbitals is shown in Table 2. To improve the quality of the bases for light atoms, scale factors were used for the valence orbitals. Scale factors are 1.283, 1.098, 1.102, 1.102, 0.966, 1.019, 1.073, 1.073, 0.981, and 0.950 for H(1s), C(2s), C($2p_x$), C($2p_y$), C($2p_z$), N(2s), N($2p_x$) N($2p_y$), N($2p_z$), and O(2s), respectively. The calculations were carried out using the JAMOL 3 program package with a Roothaan's open shell formulation. We adopted a modified scheme of integral approximation[42] based on semi-orthogonalized orbitals.[43–45] The values 3.0×10^{-3} and 1.0×10^{-5} a.u. were taken as the threshold ones, respectively, for the overlap and exchange integrals from the results of the previous studies.[42–45] The calculation of molecular integrals and supermatrices took about 5 h of CPU time on a HITAC M-180 computer at the Computer Center of the Institute for Molecular Science. The HITAC M-180 is faster in speed by a factor of 1.5 as compared with that of an IBM 370-168. Each iteration in the SCF procedure took about 2 min. Iterations were performed to obtain SCF convergence, the criterion of which was less than 1.0×10^{-6} a.u. and 5.0×10^{-4} in the maximum differente between input and output values of the total energy

TABLE 1(B). ORBITAL EXPONENTS (α) AND CONTRACTION COEFFICIENTS OF THE CGTO'S FOR H, C, N, AND O

Atom	α	Contraction coefficients of CGTO's		
		1s	2s	2p
H	4.5018	0.070452		
	0.681444	0.407826		
	0.151398	0.647752		
C	1412.29	0.004813		
	206.885	0.037267		
	45.8498	0.172403		
	12.3887	0.459261		
	3.72337	0.456185		
	0.524194		0.522342	
	0.163484		0.594186	
	4.18286			0.112194
	0.851563			0.466227
	0.199206			0.622569
N	2038.41	0.004479		
	301.689	0.034581		
	66.463	0.164263		
	17.8081	0.453898		
	5.30452	0.468979		
	0.764993		0.513598	
	0.234424		0.605721	
	5.95461			0.119664
	1.23293			0.474629
	0.286752			0.611142
O	2714.89	0.004324		
	415.725	0.032265		
	91.9805	0.15641		
	24.4515	0.447813		
	7.22296	0.481602		
	1.06314		0.504708	
	0.322679		0.616743	
	7.75579			0.129373
	1.62336			0.481269
	0.36503			0.604484

and density matric elements, respectively.

Results

The $3d_{z^2}$, $3d_{xz}$, $3d_{yz}$ orbitals of iron and $1\pi_g$ antibonding orbitals of dioxygen play important roles in the iron-oxygen bond. The π_g orbitals which are degenerate in the oxygen molecule are no longer equivalent in the complex with a bent structure. They are separated into two distinguished orbitals which are labeled as π_g^a and π_g^b in the following. The orbital π_g^a is made of $2p_x$ and $2p_z$ orbitals of the oxygen atoms and is symmetric with respect to the Fe–O_1–O_2 plane which is a plane of symmetry, while π_g^b is made of $2p_y$ orbitals and is antisymmetric with respect to the Fe–O_1–O_2 plane. The π_g^a orbital is stabilized relatively to the π_g^b orbital by the bonding interaction with the iron.

We have studied three groups of configurations $(d_\epsilon)^6(\pi_g^a)^2$, $(d_\epsilon)^5(d_\gamma)^1(\pi_g^a)^1(\pi_g^b)^1$, and$(d_\epsilon)^5(\pi_g^a)^2(\pi_g^b)^1$, where d_ϵ stands for $d_{x^2-y^2}$, d_{yz}, d_{xy} and d_γ represents $d_z{}^2$ or d_{xy}. The closed-shell singlet state $(d_\epsilon)^6(\pi_g^a)^2$ with the $^1A'$ symmetry corresponds to an Fe(II)–O_2 formal configuration. An open-shell singlet state with the configuration $(d_\epsilon)^5(d_\gamma)^1(\pi_g^a)^1(\pi_g^b)^1$ was predicted as the main configuration in the ground state of oxyheme from the *ab initio* GVB-CI calculations on the model oxyheme system composed of O_2–Fe$(NH_2)_4$–NH_3.[29,30] The configuration $(d_\epsilon)^5(\pi_g^a)^2(\pi_g^b)^1$ corresponds to the formal Fe(III)–$O_2{}^-$ configuration.

The calculated results, summarized in Table 3, indicate that the lowest energies for the oxyheme model were obtained for a group of states having a $(d_\epsilon)^5(\pi_g^a)^2(\pi_g^b)^1$ configuration. The open-shell singlet $^1A''$ (see the footnote (c) in Table 3) with the same formal configuration to that of $^3A''$ is calculated to be only 0.001 a.u. (0.03 eV) above the triplet state. One finds the quintet open-shell states, $^5A''$, and $^5A'$ at 0.032 and 0.047 a.u. (0.87 and 1.3 eV) above the lowest triplet states, respectively. Further above 0.043 a.u. (1.2 eV) from $^5A'$, there exists the closed-shell singlet $^1A'$ which corresponds to the Pauling model. These energy levels are illustrated in Fig. 2c.

The quadrupole splitting ΔE_Q of the present oxyheme model was calculated and is listed in Table 3 with the observed values in Mössbauer spectra. The ΔE_Q was determined as follows. The nine components V_{ij} of the electric field gradient tensor were calculated and the 3×3 tensor was then diagonalized. The principal values were ordered as $|V_{ZZ}|>|V_{XX}|>|V_{YY}|$. These values were then used in the expression:

$$\Delta E_Q = (1/2)(1/-R)eQq[1+\eta^2/3]^{1/2},$$

where $q=V_{ZZ}$, $\eta=|(V_{XX}-V_{YY})/V_{ZZ}|$ $(0<\eta<1)$, R is Sternheimer shielding constant, and Q is nuclear quadrupole moment. The sign of ΔE_Q is the sign of the largest component V_{ZZ} and $(1-R)eQ$ was taken as an empirical parameter determined to be 2.07 from our previous paper.[48] The calculated values of ΔE_Q, η, and the direction of the largest component of the electric field gradient tensor are listed in Table 3. These

TABLE 2. COMPARISON OF THE ORBITAL EXPONENTS (α) AND CONTRACTION COEFFICIENTS (NOT NORMALIZED) OF THE CGTO'S FOR Fe 3d ORBITALS OF OURS WITH THOSE OF DEDIEU *et al.*

			Dedieu *et al.*'s					
Ours			Basis Set I			Basis Set II		
α	$3d_1$	$3d_2$	α	$3d_1$	$3d_2$	α	$3d_1$	$3d_2$
23.2006	0.0654		12.7344	0.15472		23.2006	0.0654	
6.13066	0.28749		3.15947	0.49782		6.13066	0.28749	
1.84927	0.51785		0.77404	0.61056		1.84927	0.51785	
0.505755		1.00000	0.20000		1.00000	0.505755	0.44311	
						0.200000		1.00000

TABLE 3. SCF TOTAL ENERGIES AND MÖSSBAUER PARAMETERS CALCULATED FOR VARIOUS CONFIGURATIONS OF MODEL OXYHEME

	Formal occupation number							SCF total energy	Mössbauer parameters		
	Fe					O_2					
State	$d_{x^2-y^2}$ a′	d_{xz} a′	d_{yz} a″	d_{z^2} a′	d_{xy} a″	π_g^a a′	π_g^b a″	a.u.	ΔE_Q	η	Direction of the principal axis[a)]
$^1A''$	2	2	2	0	0	2	0	−2444.6630	0.65	0.50	z
$^5A''$	2	1	2	1	0	1	1	.7216[b)]	−1.01	0.98	z
$^5A'$	2	2	1	1	0	1	1	.7064	1.44	0.68	y
$^1A''$[c)]	2	1	2	0	0	2	1	.7521	−1.11	0.81	y
$^3A''$	2	1	2	0	0	2	1	.7531	−1.13	0.74	y
$^3A'$	2	2	1	0	0	2	1	.7512	−1.19	0.53	x
Observed[d)]									−2.10	0.23	x or y

a) The symbols x, y, and z denote the molecular axes in Fig. 1. b) The criterion of the SCF convergence is less than 2×10^{-5} (a.u.) and 2×10^{-3} in the maximum differences between input and output values of the total energy and density matrix elements. c) This state is an open-shell singlet state, where the iron spin couples with that in the dioxygen. d) Cited from the reference 5.

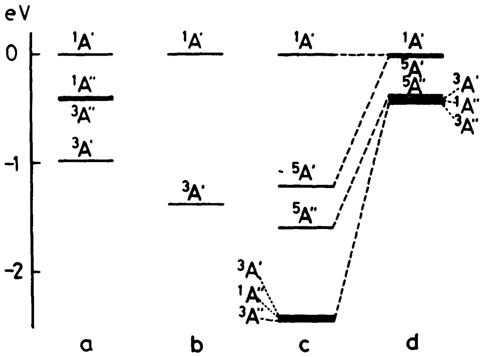

Fig. 2. The SCF energy levels for $^3A''$, $^1A''$. $^3A'$, $^5A''$, $^5A'$ and $^1A'$ from the *ab initio* LCAO-MO calculations (a—c) and the energy levels after correction of correlation energies (d).
(a). The results of Dedieu *et al.*[33—35] with the Basis Set I (minimal basis set except for the 3d orbitals with split functions).
(b). The results of Dedieu *et al.*[35] with the Basis Set II (valence double basis set).
(c). The present results with the minimal basis set except for the 3d orbitals with split functions (refer to Tables 1—3).
(d). The energy levels estimated from the present SCF energies by correction of correlation energies.[49,50]

results indicate that only the open-shell states with the configurations $(d_{x^2-y^2})^2(d_{xz})^2(d_{yz})^1(\pi_g^a)^2(\pi_g^b)^1$ and $(d_{x^2-y^2})^2(d_{xz})^1(d_{yz})^2(\pi_g^a)^2(\pi_g^b)^1$ can give ΔE_Q, and the sign and direction of the principal axis (V_{zz}) in agreement with the experimental low-temperature values ($\Delta E_Q = -2.10$ mm s^{-1}, V_{zz} in plane).[5,6]

Table 4 demonstrates the gross atomic populations and net atomic charges for the iron, oxygen and nitrogen atoms for the $^1A''$ and $^1A'$ states. As seen in Table 4, the net charges on the iron and oxygen atoms for $^1A''$ correspond well to an Fe(III)(d^5)–$O_2^-(\pi_g{}^3)$ configuration while those for $^1A'$ correspond to an Fe(II)(d^6)–$O_2(\pi_g{}^2)$ with reduced positive charge on the iron and nearly neutral oxygen atoms.

TABLE 4. GROSS AO POPULATIONS OF THE OXYHEME MODEL

AO		$^1A'$		$^1A''$	
		Population	Net charge	Population	Net charge
O_2	2s	1.89		1.88	
	$2p_z$	1.51		1.50	
	$2p_x$	1.56	0.00	1.57	−0.19
	$2p_y$	1.05		1.24	
O_1	2s	1.86		1.80	
	$2p_z$	1.54		1.36	
	$2p_x$	1.60	−0.10	1.56	−0.46
	$2p_y$	1.10		1.75	
Fe	$3d_{x^2-y^2}$	1.99		1.90	
	$3d_{xz}$	1.97		1.08	
	$3d_{yz}$	1.84		1.99	
	$3d_{z^2}$	0.15		0.40	
	$3d_{xy}$	0.24	1.23	0.37	1.50
	4s	0.23		0.27	
	$4p_z$	0.09		0.14	
	$4p_x$	0.20		0.22	
	$4p_y$	0.20		0.22	
N_{pyrr}	2s	1.53		1.15	
	$2p_z$	1.36		1.40	
	$2p_x$	1.25	−0.37	1.24	−0.38
	$2p_y$	1.25		1.24	
N_{axial}	2s	1.47		1.47	
	$2p_z$	1.80		1.78	
	$2p_x$	1.17	−0.60	1.19	−0.62
	$2p_y$	1.17		1.19	

Table 5 displays the bond overlap populations of the open-shell singlet ($^1A''$) and the closed-shell singlet ($^1A'$) states calculated by Mulliken's population analysis. The difference (0.15) in the total overlap population of the O_1–O_2 bond between the two states is related mainly to the p orbitals. This indicates that the O_1–O_2 bond of the $^1A''$ state is weakened by the excess electron population in the anti-bonding π_g^b orbital. Another important difference exists in the Fe–O_1 bond, which is non-bonding for the $^1A'$ state but bonding for the $^1A''$ state. Therefore, the Fe–O_1 bond in $^1A''$ state is more stabilized than that in the $^1A'$ state by both covalent and ionic interactions. There exist no significant differences in the overlap populations of the Fe–$N_{pyrrole}$ and the Fe–N_{axial} bonds between the two states.

Table 5. Overlap populations of the oxyheme model

Bond	Type	$^1A'$	$^1A''$
O_1–O_2	s–s	−0.20	−0.18
	s–p	0.05	0.08
	p–s	−0.02	0.00
	p–p	0.61	0.38
	Total	0.44	0.29
Fe–O_1	s–s	−0.02	0.00
	s–p	−0.02	0.02
	p–s	−0.01	0.03
	p–p	−0.02	0.07
	d–s	0.02	0.03
	d–p	0.08	0.12
	Total	0.03	0.27
Fe–N_{pyrr}	s–s	0.01	0.01
	s–p	0.03	0.04
	p–s	0.05	0.05
	p–p	0.08	0.10
	d–s	0.03	0.03
	d–p	0.05	0.06
	Total	0.25	0.29
Fe–N_{axial}	s–s	−0.00	−0.00
	s–p	0.00	0.01
	p–s	0.02	0.02
	p–p	0.05	0.07
	d–s	0.01	0.01
	d–p	0.03	0.03
	Total	0.11	0.14

Discussion

As shown in Fig. 2, the energy gap between $^1A'$ and $^3A'$, $^1A''$ or $^3A''$ in the present SCF calculation is substantially different from those obtained by Dedieu *et al.*[33–35] in the similar *ab initio* SCF-MO calculations with both a minimal set (except for 3d functions) (Basis Set I) and a valence-double basis set (Basis Set II). This difference gives contrary conclusions in the assignment of the ground state of oxyheme model. The total energy of the d^6 closed-shell configuration would be relatively more stabilized than those of the d^5 and d^6 open-shell configurations by the effect of the electron correlation. We have previously estimated that the correlation energy differences of the closed-shell configuration $(d_\varepsilon)^6(\pi_g^a)^2$ from the open-shell configurations $(d_\varepsilon)^5(\pi_g^a)^2(\pi_g^b)^1$, and $(d_\varepsilon)^5(d_\gamma)^1(\pi_g^a)^1(\pi_g^b)^1$ would be ≈2.0 eV[49] and ≈1.2 eV,[50] respectively. Figure 2d illustrates the effect of the electron correlation on the open-shell configurations relative to the closed-shell one. As seen from Fig. 2d, the lowest state is one with the open-shell configuration Fe(III)$(d_\varepsilon{}^5)$–$O_2{}^-(\pi_g{}^3)$, even after consideration for the correlation energy. The open-shell state $^3A''$ with the configuration Fe(II)$(d_\varepsilon{}^5 d_\gamma{}^1)$–$O_2(\pi_g{}^2)$ stays just above those with the $(d_\varepsilon)^5(\pi_g)^3$ configurations, and another open-shell quintet state $^5A'$ lies close to the closed-shell $^1A'$ state in Fig. 2d.

In the calculations with basis set I and II by Dedieu *et al.*[33–35] the energies of the closed-shell state ($^1A'$) are only 0.036 a.u. (0.98 eV) and 0.051 a.u. (1.39 eV), respectively above those of the open-shell state ($^3A'$). They concluded that the closed-shell state ($^1A'$) is the ground state because the SCF energy gap of the two states is smaller than the difference in the correlation energy.

The reason why the SCF energy gap is larger in the present calculation than in their calculations comes from the contents of the basis functions, since the present calculation employed the same oxyheme model as that of Dedieu *et al.*[33–35] Between the present basis set and Dedieu's basis set I, there is no fundamental difference except for the 3d functions. They do differ significantly in the split between ours and those of Dedieu *et al.* as listed in Table 2. Dedieu *et al.* incremented primitive Gaussian functions with an exponent of 0.20 to the atomic 3d orbitals optimized for the iron atom, while we divided the original atomic 3d orbitals into two components (d_1 and d_2) composed of 3 and 1 primitive Gaussian functions, the latter of which has a exponent of 0.505755. Our choice is based on the following argument. In our calculation on cobalt porphine with a triple zeta basis for 3d orbitals[36] the most diffuse d function with an exponent of 0.18 was not effective, while the d function with an exponent of 0.555999 was very important in the proper description of the molecular orbitals. The present form of the split could take account of the effect of the contraction of the 3d orbitals in the change from iron(II) (in $^1A'$) to iron(III) (in $^1A''$). In Table 6, the ratio of coefficients of the two 3d functions (d_1/d_2) is shown for each molecular orbital. The ratios for the iron(II) state are not very different from the ratio of 1.67 for the atomic orbital of the neutral iron. This means that the 3d components in the iron(II) state are as well described as in the iron atom. The large values of the ratio in the iron(III) state indicate the contraction of the 3d components. Therefore the form of the split by Dedieu *et al.*[33–35] is not adequate to describe the iron(III) states, even if it is acceptable for a description of the iron(II) states.

From the observed predominant diamagnetism of oxyhemoglobin and of the dioxygen complex of the picket fence porphyrin, the ground state is assigned to the open-shell singlet $^1A''$ in the present SCF calculation. A strong support for this assignment of the ground state comes from the calculation of the Mössbauer parameters. As shown in Table 3, the open-shell singlet state $^1A''$ yields a large negative electric field gradient whose direction is in the heme plane. These calculated results are in good agreement with low temperature measurements of the single crystal Mössbauer resonance of oxyhemoglobin.[5,6] On the contrary, the closed-shell singlet state $^1A''$, which was assigned as the ground state of the oxyheme by Dedieu *et al.*, can not yield correct Mössbauer parameters, as is seen in Table 3, and as was also shown previously.[27] It should be added that the quintet states do not yield Mössbauer parameters consistent with the low temperature experimental values (Table 3).

The $^1A''$ state can be regarded as a $d\pi$-π_g charge-transfer state of $^1A'$ and has the iron(III) superoxide character as shown in Table 4. This arises from an appreciable amount of charge-transfer from the iron atom to the dioxygen ligand. One electron is transferred from the iron d_{xz} orbital to the oxygen anti-bonding

Table 6· Comparison of the coefficients of the molecular orbitals with predominant 3d character and the ratios ofthose for $^1A'$ with those for $^1A''$

MO	$^1A'$ Coefficient (d_1/d_2 Ratio)	Energy a.u.	MO	$^1A''$ Coefficient (d_1/d_2 Ratio)	Energy a.u.
57a′ $(d_{xz})_1$	0.4045		42a′ $(d_{xz})_1$	0.7318	
$(d_{xz})_2$	0.2472	−0.4520	$(d_{xz})_2$	0.3809	−0.6621
	(1.63)			(1.92)	
58a′ $(d_{xz})_1$	0.4147		28a″ $(d_{yz})_1$	0.5786	
$(d_{xz})_2$	0.2537	−0.4394	$(d_{yz})_2$	0.3215	−0.6379
	(1.63)			(1.80)	
59a′ $(d_{x^2-y^2})_1$	0.6194		44a′ $(d_{x^2-y^2})_1$	0.4804	
$(d_{x^2-y^2})_2$	0.3789	−0.4365	$(d_{x^2-y^2})_2$	0.2661	−0.6213
	(1.63)			(1.81)	
39a″ $(d_{yz})_1$	0.6076				
$(d_{yz})_2$	0.3926	−0.4212			
	(1.55)				

orbital. The ligands donate approximately one electron (0.77) to the formally empty d_{z^2} and d_{xy} orbitals (Table 4). Furthermore the iron 4s and 4p orbitals receive approximately one electron (0.85) from the ligands. This results in atomic charges of 1.50 on the iron atom and −0.65 on the dioxygen ligand in the $^1A''$ state (Table 4).

The following conclusions were obtained from the present *ab initio* LCAO-SCF-MO calculations of the oxyheme model on several singlet, triplet, and quintet states, which arise from the three types of configurations, $(d_\varepsilon)^6(\pi_g^a)^2$, $(d_\varepsilon)^5(d_\gamma)^1(\pi_g^a)^1(\pi_g^b)^1$, and $(d_\varepsilon)^5(\pi_g^a)^2(\pi_g^b)^1$. The lowest states in the SCF energy have the configuration $(d_\varepsilon)^5(\pi_g^a)^2(\pi_g^b)^1$ whose electronic structure can be expressed as $Fe(III)-O_2^-$ from the results of Mulliken's population analysis. This configuration remains as the lowest energy states even after consideration of the correlation energy. Calculated Mössbauer parameters of these states are in good agreement with experiments for oxyhemoglobin, oxymyoglobin and oxyheme model, while those of the closed-shell singlet state $(d_\varepsilon)^6(\pi_g^a)^2$ are inconsistent with experiment. The $Fe-O_1$ overlap populations indicate a bonding nature for the $(d_\varepsilon)^5(\pi_g^a)^2(\pi_g^b)^1$ states and a non-bonding nature for the $(d_\varepsilon)^6(\pi_g^a)^2$ state. From the above discussion, the open-shell singlet state $^1A''$, $(d_\varepsilon)^5(\pi_g^a)^2(\pi_g^b)^1$, is the most promising candidate for the ground state of the oxyheme model in the framework of the present Hartree-Fock level calculation. However the ground state and low-lying states would need to be described as a more complex wavefunction than a sigle configuration function if we consider the configuration interaction, the spin-orbit interaction, and the lack of C_s symmetry. Our results indicate singlet configurations $(d_\varepsilon)^5(\pi_g)^3$ with the $Fe(III)-O_2^-$ structure as the most important configurations of the ground state in the oxyheme model.

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References

1) J. P. Collman, R. R. Gagne, C. A. Reed, W. T. Robinson, and G. A. Rodley, *Proc. Natl. Acad. Sci. U. S. A.*, **71**, 1326 (1974).

2) S. E. V. Phillips, *Nature (London)*, **273**, 247 (1978).

3) L. Pauling, *Nature (London)*, **203**, 182 (1964).

4) G. Lang and W. Marshall, *Proc. Phys. Soc.*, **87**, 3 (1966).

5) K. Spartalian and G. Lang, *J. Chem. Phys.*, **63**, 5375 (1975).

6) Y. Maeda, T. Harami, Y. Morita, A. Trautwein, and U. Gonser, *J. Chem. Phys.*, **75**, 36 (1981).

7) J. P. Collman, R. R. Gagne, C. A. Reed, T. R. Halbert, G. Lang, and W. T. Robinson, *J. Am. Chem. Soc.*, **97**, 1427 (1975).

8) M. W. Makinen and W. A. Eaton, *Ann. N. Y. Acad. Sci.*, **206**, 210 (1973).

9) W. A. Eaton, L. L. Hanson, P. J. Stephens, J. C. Sutherland, and J. B. R. Dunn, *J. Am. Chem. Soc.*, **100**, 4991 (1978).

10) M. Hatano and T. Nozawa, *Adv. Biophys.*, **11**, 95 (1978).

11) J. C. Maxwell, J. A. Vople, C. H. Barlow, and W. S. Caughey, *Biochem. Biophys. Res. Commun.*, **58**, 166 (1974).

12) C. H. Barlow, J. C. Maxwell, W. C. Wallace, and W. S. Caughey, *Biochem. Biophys. Res. Commun.*, **55**, 91 (1973).

13) J. P. Collman, J. I. Brauman, T. R. Halbert, and K. S. Suslick, *Proc. Natl. Acad. Sci. U. S. A.*, **73**, 333 (1976).

14) A. Barbe, C. Secrauer, and P. Jonve, *J. Mol. Spectrosc.*, **49**, 171 (1974).

15) T. Yamamoto, G. Palmer, D. Gill, I. T. Salmen, and L. Rimai, *J. Biol. Chem.*, **248**, 5211 (1973).

16) A. Debois, M. Lutz, and R. Banerjee, *Biochem.*, **18**, 1510 (1979).

17) M. Cerdonio, A. Congiu-Castellano, F. Mogno, B. Pispisa, G. L. Romani, and S. Vitale, *Proc. Natl. Acad. Sci. U. S. A.*, **74**, 398 (1977).

18) L. Pauling and C. D. Coryell, *Proc. Natl. Acad. Sci. U. S. A.*, **22**, 210 (1936).

19) C. D. Coryell, L. Pauling, and R. W. Dodson, *J. Phys. Chem.*, **43**, 825 (1939).

20) D. S. Taylor and C. D. Coryell, *J. Am. Chem. Soc.*, **60**, 1177 (1938).

21) L. Pauling, *Proc. Natl. Acad. Sci. U.S.A.*, **74**, 2612(1977).

22) M. Cerdonio, A. Congiu-Castellano, L. Cal bress, S. Morante, B. Pispisa, and S. Vitale, *Proc. Natl. Acad. Sci. U. S. A.*, **75**, 4916 (1978).

23) A. S. Koster, *J. Chem. Phys.*, **56**, 3161 (1972).

24) M. Zerner, M. Gouterman, and H. Kobayashi, *Theor. Chim. Acta*, **6**, 363 (1966).

25) M. Halton, *Theor. Chim. Acta*, **24**, 89 (1972).

26) R. R. Kirchner and G. H. Loew, *J. Am. Chem. Soc.*, **99** 4639 (1977).

27) B. H. Huynh, D. A. Case, and M. Karplus, *J. Am. Chem. Soc.*, **99**, 6103 (1977).

28) D. A. Case, B. H. Hynh, and M. Karplus, *J. Am. Chem. Soc.*, **101**, 4433 (1979).

29) W. A. Goddard and B. D. Olafson, *Proc. Natl. Acad. Sci. U. S. A.*, **72**, 2335 (1975).

30) B. D. Olafson and W. A. Goddard, *Proc. Natl. Acad. Sci. U. S. A.*, **74**, 1315 (1977).

31) Z. S. Herman and G. H. Loew, *J. Am. Chem. Soc.*, **102**, 1815 (1980).

32) Y. Seno, J. Otsuka, O. Matsuoka, and N. Fuchikami, *J. Phys. Soc. Jpn.*, **33**, 1645 (1972).

33) A. Dedieu, M.-M. Rohmer, and A. Veillard, "Proceeding of the 9th Jerusalem Symposium on Quantum Chemistry and Biochemistry, March 29—April 2, 1976, Metal-Ligand Interactions in Organic Chemistry and Biochemistry," ed by B. Pullman and N. Goldblum, D. Reidel, Holland (1977), p. 101.

34) A. Dedieu, M.-M. Rohmer, and A. Veillard, *J. Am. Chem. Soc.*, **98**, 5789 (1976).

35) A. Dedieu, M.-M. Rohmer, H. Veillard, and A. Veillard, *Nouv. J. Chim.*, **3**, 653 (1978).

36) H. Kashiwagi, T. Takada, S. Obara, E. Miyoshi, and K. Ohno, *Int. J. Quant. Chem.*, **14**, 13 (1978).

37) S. M. Peng and J. A. Ibers, *J. Am. Chem. Soc.*, **98**, 8032 (1976).

38) W. S. Benedict and E. L. Plyler, *Can. J. Phys.*, **35**, 1235 (1975).

39) B. Roos, G. Vinat, and A. Veillard, *Theor. Chim. Acta*, **20**, 1 (1971).

40) B. Roos and P. Siegbahn, *Theor. Chim. Acta*, **17**, 209 (1970).

41) The library program of the Computer Center of Institute for Molecular Science which was coded by H. Kashiwagi, T. Takada, E. Miyoshi, S. Obara, and F. Sasaki, and reported in the paper (H. Kashiwagi and S. Obara, *Int. J. Quant. Chem.*, **20**, 843 (1981)).

42) Y. Osanai and H. Kashiwagi, *Int. J. Quant. Chem.*, **17**, 103 (1980).

43) H. Kashiwagi, *Int. J. Quant. Chem.*, **10**, 135 (1976).

44) H. Kashiwagi and T. Takada, *Int. J. Quant. Chem.*, **12**, 449 (1977).

45) H. Kashiwagi and F. Sasaki, *Int. J. Quant. Chem., Symp.*, **7**, 515 (1973).

46) The present SCF program can not deal with more than two open-shells of the same irreducible representations except for states with parallel spins in all the open-shells.

47) J. J. Weiss, *Nature (London)*, **202**, 83 and 183 (1964).

48) S. Obara and H. Kashiwagi, *J. Chem. Phys.*, **77**, 3155 (1982).

49) The correlation energy was estimated from the differences between calculated and experimental transition energies. The well characterized charge-transfer transition for metmyoglobin cyanide at 6.4×10^3 cm^{-1} (0.79 eV)[51] was utilized for this purpose. Our *ab initio* calculation with a partial-double basis on (porphinato)iron(III)(py)(CN$^-$) yielded the excited state $^2A_1$ $((d_{x^2-y^2})^2(d_{xz})^2(d_{yz})^2(a_{1u})^2(a_{2u})^1)$ (a d^6 state) at 2.80 eV above the ground state $^2B_2$ $((d_{x^2-y^2})^2(d_{xz})^2(d_{yz})^1(a_{1u})^2(a_{2u})^2$ (a d^5 state) (unpublished results). The difference (2.01 eV) between the calculated transition energy (2.80 eV) and the experimental one (0.79 eV) should be the correlation bias between d^5 states and d^6 states which is the predominant correlation energy difference between $^3A'$, $^3A''$ or $^1A''$, and $^1A'$.

50) The correlation energy between the $^5A'$ or $^5A''$ and $^1A'$ was estimated from the difference between the *ab initio* SCF energies calculated for (porphinato)iron(II)(py) with a partial-double basis[48] and the energy diagram determined by Eicher and Trautwein for deoxyhemoglobin.[52]

51) T. Nozawa, T. Yamamoto, and M. Hatano, *Biochim. Biophys. Acta*, **427**, 28 (1976).

52) H. Eicher and A. Trautwein, *J. Chem. Phys.*, **50**, 2540 (1969).