

Effect of the fifth coordination site on the spin states of bis(benzoylacetylacetonato)bispyridinedicopper(II) complex

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Received 11 February 1993; in final form 4 June 1993

The spin and charge excitation gap and spin density have been calculated for bis(benzoylacetylacetonato)bispyridinedicopper(II) using a valence bond basis and model Hamiltonian based on the Pariser–Parr–Pople (PPP) approximation. The singlet–triplet energy gap depends upon the exchange interaction (K_{OO}) of the bridging oxygen atom. The results of this 12-orbital, 18-electron system are compared with those of a 10-orbital, 14-electron system, viz. bis(benzoylacetylacetonato)dicopper(II), the latter without axial ligation. Changing the nitrogen to oxygen in the fifth coordination site does not seem to affect the singlet–triplet energy gap and spin and charge density on the copper(II) atoms. The results indicate that K_{OO} , which is sensitive to geometry, plays a decisive role in determining the excitation gap.

1. Introduction

Understanding the mechanism for exchange interaction between metal centers in polymetallic complexes has been a subject of sustained interest. Exchange coupled systems, both antiferromagnetic and ferromagnetic, have been studied experimentally by a variety of spectroscopic techniques and magnetic susceptibility measurements. There have been many successful attempts to correlate the magnetic properties with structural details of these complexes. For instance, an empirical equation has been developed by Hatfield [1] for binuclear Cu(II) species correlating S–T (singlet–triplet) energy gap with bridging angle ϕ (M–L–M),

$$\Delta E_{ST} = -74.53 (\text{cm}^{-1} \text{deg}^{-1})\phi(\text{deg}) + 7270 (\text{cm}^{-1}). \quad (1)$$

Similar equations have been employed to explain such energy gaps in dimers of nickel dithiolene molecules [2]. However, a deeper understanding has emerged from the work of Anderson [3], Goodenough [4], Kanamori [5] and Hay et al. [6].

Ginsberg [7] had shown that density functional MO theory ($X\alpha$ -SW) was also useful for studying exchange interactions in transition-metal dimers. Hay et al. [6] defined J in the Hückel framework as follows:

$$J = K_{ab} - (\epsilon_S - \epsilon_A)^2 / (J_{aa} - J_{ab}), \quad (2)$$

where K_{ab} is the exchange integral (potential exchange) and ϵ_S and ϵ_A are the one-electron energies of the symmetric and antisymmetric MOs formed from the magnetic orbitals of each of the interacting copper atoms. Bencini and Gatteschi [8] applied the orbital angular overlap approach to dimeric copper(II) complex and obtained results similar to those of Hay et al. Kahn et al. [9] described the S–T splitting as a sum of antiferromagnetic and ferromagnetic contributions described by

$$J = J_{AF} + J_F, \quad J_{AF} = -2\Delta S, \quad J_F = 2C, \quad (3)$$

where S is the overlap integral between the two magnetic orbitals σ_A and σ_B originating from the two metal centers, Δ is the energy gap between the two molecular orbitals formed from them and C is the two-electron exchange integral. Kettle and Tsaparlis

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[10] obtained qualitative information about some parameters that influence the exchange interaction in aromatic-N-oxide bridged copper(II) complexes using an INDO treatment. The most serious calculations on exchange interactions have been from de Loth and co-workers [11] using ab initio calculations and Noodleman [12] employing the X- α approach. Ab initio calculations on such large systems would, in general, require many orbitals as well as many configurations and would make the computation prohibitively time consuming [13]. The optimal choice appears to center around a full-CI calculation of a model Hamiltonian using only the orbitals participating in the σ bonds between the metal ions and the ligand atoms. The success of this approach will depend on the parameters of such a model Hamiltonian. Nonetheless, it is fortuitous that the interest in the copper-based high- T_c ceramic superconductors has led to a reasonable set of parameters for copper and oxygen atoms. Hence, this can serve as a good starting point for model calculations [14] involving copper ions. Our earlier report using this approach on a few model systems [15] confirms the suitability of such parameters. In that report, we discussed the results on aza-amido systems containing 12, 14 and 16 electrons. This calculation included the orbitals on the nearest neighbours of the copper ions involved in a σ -type bonding with the $d_{x^2-y^2}$ orbitals of copper using a valence bond (VB) basis and model PPP Hamiltonian. In our present work, we have extended our calculation to 10-orbital, 14-electron systems containing only oxygen both for terminal and bridging atoms (I in fig. 1) for comparing with similar systems with nitrogens as terminal atoms (model complex II) of our earlier report [15]. Also reported are calculations on the ligands and metals moieties of two complexes [16] viz. bis(benzoylacetylacetonato)bis(pyridine)dicationic copper(II) and bis[2,5-bis(trifluoroacetyl)cyclopentanato]dicopper(II) hydrate (II and III of fig. 1). The latter two are modifications of structure I in fig. 1 with nitrogens and oxygens as fifth coordination sites on the central copper atoms. In these, we deal with a total of 12 orbitals (sites) and 18 electrons. The number of electrons are calculated with contributions of 1 and 2 electrons, respectively, from covalent and coordinate bonds associated with the

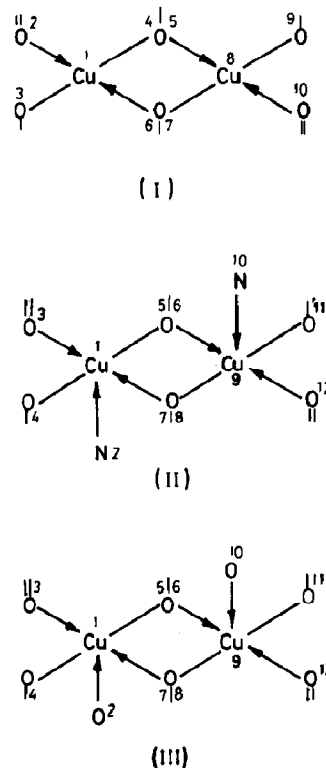


Fig. 1. Structures of 10-orbital, 14-electron model complex, I and 10-orbital, 18-electron model complexes, II and III. Arrows indicate coordinate bonding.

nearest-neighbour ligands and one electron from the $d_{x^2-y^2}$ orbitals of each copper(II) ion. For Q electrons with spin $S \leq Q/2$ or $N \geq Q/2$ sites, the number of Rumer-Pauling diagrams P_S depicting the VB connectivity for each $S_z = S, S-1, \dots, -S$ is given by the Weyl formula [17,18]

$$P_S = \frac{2S+1}{N+1} [(N+1)C_{Q/2-S} (N+1)C_{N-Q/2-S}], \quad (4)$$

where $()$ is a binomial coefficient. Accordingly, for structure I in fig. 1, the complete singlet manifold spanned is 4950 while for the triplet and quintet manifolds these dimensionalities are, respectively, 6930 and 2310. However, for systems II and III the dimensionalities of the singlet, triplet and quintet

states are 15730, 23166 and 8580, respectively.

The theoretical calculations are carried out by employing a VB basis with an interacting Hamiltonian that includes electron repulsions parametrically within the zero differential overlap (ZDO) approximation. The low-lying states and their properties are obtained by solving the model Hamiltonian exactly to all orders in CI within the restricted basis. These model Hamiltonians after parametrization have been found to predict the experimental properties of the low-lying states with reasonable accuracy [19–21]. Such parameters have been found to be transferable from one molecule to another [20,21]. Similarly, the range of these parameters for predicting the properties of copper d orbitals are well formulated [20] and justify studying the properties of the electronic states of copper complexes containing nitrogen and oxygen ligands in any hybridization using this methodology [20,21]. The other parameters in the exchange coupled binuclear species are metal–ligand bond distances and metal–ligand–metal bond angles and the metal–metal distances. For example, the ground state changes its spin multiplicity at a critical M–L–M bond angle of 97.68° [22,23].

2. Model Hamiltonian and computational details

For systems under consideration in this work (fig. 1) the many-body Hamiltonian consists of orbitals on the adjacent atoms of the copper ions involved in a σ -type bonding with $d_{x^2-y^2}$ orbitals of the copper ions. For system I, we have used 10 orbitals and 14 electrons, the model Hamiltonian being similar to that in eq. (1) of ref. [15]. For the two complex species (II and III) we deal with 12 orbitals and 18 electrons. The PPP Hamiltonian over this orbital basis within the ZDO approximation in the second quantized notation is given by [24,25]

$$\begin{aligned} \mathcal{H} = & \sum_i \epsilon_i \hat{n}_i + \sum_{\langle ij \rangle} \sum_{\sigma} t_{ij} (a_{i\sigma}^* a_{j\sigma} + \text{h.c.}) \\ & + \frac{1}{2} \sum_i U_i \hat{n}_i (\hat{n}_i - 1) \\ & + U_{\text{OO}} [(\hat{n}_5 - z_5)(\hat{n}_6 - z_6) + (\hat{n}_7 - z_7)(\hat{n}_8 - z_8)] \\ & + K_{\text{OO}} [(\hat{E}_{56} + \hat{E}_{65})^2 + (\hat{E}_{78} + \hat{E}_{87})^2 \\ & - \hat{n}_5 - \hat{n}_6 - \hat{n}_7 - \hat{n}_8] \\ & + \sum_{i>j} V_{ij} (\hat{n}_i - z_i) (\hat{n}_j - z_j), \end{aligned} \quad (5)$$

where ϵ_i is the site (orbital) energy of the site (orbital) i , n_i is the occupation number operator for the orbital i , t_{ij} is the transfer integral for the bond connecting adjacent atoms, $a_{i\sigma}^*$ ($a_{i\sigma}$) creates (annihilates) an electron with spin σ in the i th orbital and h.c. corresponds to Hermitian conjugate. The transfer integrals for Cu–O and Cu–N bonds are parametrized at 1.30 and 1.50 eV, respectively. The value for Cu–O at this distance has been established in the context of high- T_c superconductors [21] and that for Cu–N is fixed by taking into account the less compact nature of nitrogen atomic orbitals and small difference in the Cu–N distance. The values for electron repulsion integral U_i , between the electrons for the $d_{x^2-y^2}$ orbitals of copper and those of oxygen and nitrogen orbitals, are already established. The optimal value for the Coulomb integral, U_{OO} , is 6.00 eV and that for the exchange integral, K_{OO} , involving two orbitals on the same oxygen atoms varied between 0.0 and -0.4 eV. The K_{OO} value will depend sensitively upon the hybridisation of the oxygen orbitals and thus on the M–O–M bond angle. The operator $E_{ij} = (a_{i\alpha}^* a_{j\alpha} + a_{i\beta}^* a_{j\beta})$ is the electron transfer operator that hops an electron from orbital j to orbital i . V_{ij} is the interaction energy between an electron in orbital i on one atom and an electron on orbital j on another atom and is parametrized following Ohno [26]:

$$V_{ij} = 14.397 \{ [28.794 / (U_i + U_j)]^2 + r_{ij}^2 \}^{-1/2}. \quad (6)$$

Furthermore, z_i is the occupancy of the site i required to leave the site electrically neutral. The Ohno parametrization extrapolates the repulsion integral between U for $r_{ij}=0$ and e^2/r_{ij} for large r_{ij} . Parameters used for the geometries of the three complexes (fig. 1) are given in table 1.

Table 1

Values of different parameters appearing in the PPP Hamiltonian in eq. (5). U_{OO} is fixed at 6.00 eV and K_{OO} is varied from 0.0 to -0.4 eV. The σ orbitals on the primed atoms are doubly occupied

	ϵ (eV)	U (eV)	z
O	-2.0	15.5	1
O'	-14.0	15.5	2
N'	-12.0	15.0	2
Cu	0.00	12.0	1

The PPP Hamiltonian conserves total spin and we have used a diagrammatic VB basis for obtaining the Hamiltonian matrix. A complete and linearly independent VB basis can be generated by employing modified Rumer–Pauling rules [27] and can be stored in the computer as integers in an increasing sequence using pairs of bits in the integer to level the state of each orbital. The Hamiltonian matrix is set up by operating with the Hamiltonian on the VB functions in succession and storing the coefficients of the resulting VB functions. These complexes are not topologically one-dimensional and hence involved electron transfers between non-consecutively labelled orbitals. Such orbital transfers lead to generation of “illegal” diagrams^{#1} violating Rumer–Pauling rules. While generation of such “illegal” diagrams can be avoided by using the commutation relation,

$$E_{ij} = [E_{ik}, E_{kj}] - ,$$

where *k* is an intervening orbital, it is CPU intensive and we resort to a different technique, described in detail elsewhere [28,29].

3. Results and discussion

We report here calculations on (i) a cluster of 8 atoms of a dinuclear copper(II) species in which both terminal and bridging atoms are oxygens (model I of fig. 1) and (ii) a cluster of 10 atoms of two other dinuclear copper(II) species II and III of fig. 1 which are modifications of I with axial coordinations with nitrogen and oxygen, respectively. Only the σ orbitals of the ligands are considered bonded to the $d_{x^2-y^2}$ orbital of copper(II). While the bridging oxygens are sp^3 hybridised, the terminal and axial oxygens are sp^3 or sp^2 hybridised. The nitrogen atoms in the axial site of complex II are sp^2 hybridised. The ligands connected by covalent bonds provide one electron each and those by coordinate bonds two electrons each, while the $d_{x^2-y^2}$ orbitals of Cu(II) provide one each. Complex I is thus a 10-orbital, 14-

electron system and II and III are 12-orbital, 18-electron systems. Molecules of types I, II and III have been observed experimentally [16].

We have studied theoretically the following properties: energies of low-lying singlet, triplet and quintet states and charge and spin densities where applicable. As in earlier work [15] these properties have been studied as functions of exchange integrals involving two hybridised oxygen orbitals on the same atom, viz. K_{OO} . In one set of calculations, uniform transfer integrals equal to 1.40 eV have been employed for all bonded orbitals.

In another set, transfer integral values of 1.50 and 1.30 eV have been employed, respectively, for Cu–N and Cu–O bonds to justify the difference in bond lengths and atomic numbers of ligands, especially for model II. The atomic coordinates of the models are entered into the calculation through the intersite potential terms. The geometry for complexes II and III was taken from the literature [16] while that for I was taken from our earlier work on the corresponding system with nitrogens as terminal atoms. All other parameters except K_{OO} (needed for the work) are fixed at literature values [16,19–21].

Experimentally, all complexes corresponding to models I to III have singlet ground states [16] which is supported by the present calculations independent of K_{OO} values. In accordance with the trend expected from our earlier work [15], with model parameters given in table 1 and $K_{OO}=0$, the singlet and triplet states are degenerate in all three systems and the energy gaps ϵ_{ST} (singlet–triplet) and ϵ_{SQ} (singlet–quintet) vary linearly with K_{OO} with opposite signs for the slope. The calculated spin gaps and their dependence on K_{OO} for all complexes and charge and spin densities for a single value of $K_{OO}=0.0$ eV are given in tables 2, 3, and 4. When a small negative value of K_{OO} is turned on, the degeneracy of ϵ_{ST} is removed. Upon further increase in the magnitude of K_{OO} , with sign kept negative, the singlet–triplet excitation gap becomes largest at the largest absolute value of K_{OO} for all complexes. Furthermore, for a given value of the exchange interaction, K_{OO} , the model complexes II and III with axial ligand yield a higher ϵ_{ST} than that for I without axial ligation, viz. for a value for K_{OO} of -0.4 eV, we have ϵ_{ST} values of 201, 213 and 215 cm^{-1} for I, II and III. Ref. [16] and those cited therein indicate such a trend, i.e. those without axial

^{#1} Illegal diagrams are those with intersections of lines and can be resolved, or expanded, in terms of legal diagrams. Legal diagrams form a complete, linearly independent basis.

Table 2

Energy gaps in cm^{-1} as a function of K_{OO} (eV) in complexes I to III at various values of K_{OO} and the same transfer integrals

K_{OO}	I		II		III	
	ϵ_{ST}	ϵ_{SQ}	ϵ_{ST}	ϵ_{SQ}	ϵ_{ST}	ϵ_{SQ}
0.0	0.00	9134	0.0	10537.76	0.00	10407.96
-0.1	37.06	9117	43.94	10413.20	44.43	10334.77
-0.2	92.83	9114	100.56	10242.17	93.62	10245.47
-0.3	126.24	9106	160.27	10131.85	150.23	10134.99
-0.4	201.43	9109	212.56	8889.76	214.58	10003.83

Table 3

Charge densities at different atoms in complexes I to III in singlet, triplet and quintet states for $K_{\text{OO}}=0.00$ eV

Atom	I			II			III		
	S=0	S=1	S=2	S=0	S=1	S=2	S=0	S=1	S=2
Cu	1.081	1.061	1.124	1.092	1.096	1.157	1.089	1.095	1.140
O ^{a)}	1.939	1.938	1.929	1.940	1.941	1.932	1.939	1.940	1.914
O ^{b)}	1.023	1.022	1.013	1.038	1.036	1.020	1.033	1.034	1.026
O ^{c)}	2.956	2.956	2.953	2.973	2.971	2.940	2.966	2.956	2.930
N ^{d)}				1.957	1.954	1.951	-	-	-
O ^{d)}				-	-	-	1.971	1.967	1.961

a) Terminal oxygen with coordinate bond.

b) Terminal oxygen with covalent bond.

c) Bridging oxygen.

d) Fifth coordination site.

Table 4

Spin densities at different atoms in complexes I to III for $K_{\text{OO}}=0.0$ eV

Atom	I		II		III	
	S=1	S=2	S=1	S=2	S=1	S=2
Cu	-0.243	0.298	-0.2218	0.3436	-0.2266	0.3458
O ^{a)}	-0.019	0.031	-0.0175	0.0343	-0.0182	0.0104
O ^{b)}	0.640	0.816	0.6419	0.8334	0.6402	0.7916
O ^{c)}	0.616	0.855	0.6102	0.8585	0.6169	0.8406
N ^{d)}			-0.0128	0.0215	-	-
O ^{d)}			-	-	-0.0120	0.0125

a) Terminal oxygen with coordinate bond.

b) Terminal oxygen with covalent bond.

c) Bridging oxygens with covalent bond.

d) Fifth coordinate site.

ligation have J values of -200 to -280 cm^{-1} while those with axial ligands have values from -345 to -370 cm^{-1} . Though we are unable to predict the precise experimental values, it is gratifying to note

that the order of magnitude and trend is apparent from our calculations.

While the magnitude of ϵ_{ST} is small and its dependence on K_{OO} is substantial, ϵ_{SQ} is high and in the

range 9000–10000 cm^{-1} but its percentage change with K_{OO} is minimal. High ϵ_{SQ} gaps for all systems are indicative of spin-density redistribution as borne out by the spin-density results in table 4 (*vide infra*). In general, the absolute values for spin excitation gaps are large for the axially modified systems **II** and **III**.

The charge density data for all three complexes indicate no surprise or drastic change, as seen in table 3. The charge distribution remains approximately the same for all spin states within a given complex similar to our earlier observation [15]. The present charge density results, combined with those from our earlier work [15], confirm our observation on spin-wave and Stoner excitations [30] and their relation to our binuclear coupled systems.

In contrast to charge density, the spin-density distributions (table 4) in these three complexes are interesting. Only in the case of triplets, both the copper atoms and all sites providing two electrons (i.e. coordinate bond) have residual amounts of negative spin density while a large excess of positive spin density is found on the other terminal (providing covalent bond) and bridging oxygen. However, the spin-density distributions in the quintet states of all molecules are distinctly different from those in the triplet in more than one way. First, all atoms have positive densities. Second, the spin-density distributions on various atoms are different in quintet states in comparison to triplet states. Axial ligation on copper seems to be responsible for the increased spin density on copper due to the quintet state. The largest spin densities are found on bridging oxygens and the terminal oxygen with covalent bond in addition to copper, indicating the possibility of spin-wave excitation associated with ϵ_{SQ} . Furthermore, the

spin densities are insensitive to changes in the K_{OO} parameter, like the absolute energies of different states.

The energy gaps between states of the same spin multiplicity in axially ligated complexes **II** and **III** have been calculated as functions of K_{OO} . Table 5 shows the variation of singlet–singlet (ϵ_{SS}), triplet–triplet (ϵ_{TT}), quintet–quintet (ϵ_{QQ}) energy separations. For both complexes **II** and **III**, ϵ_{SS} increases with the increase of $-K_{\text{OO}}$ while ϵ_{TT} behaves in the reverse way. The ϵ_{QQ} value is small for both complexes and though it increases with increasing $-K_{\text{OO}}$ value, the excited quintet states essentially remain degenerate. The energy spectra for **II** and **III** are basically the same and in conformity with that of **I**. The spectral energy variation for **I** is shown in fig. 2.

A study of energy gaps with nonuniform and uniform transfer integrals for Cu–N and Cu–O in complex **II** indicates small changes as in table 6. Generally, the nonuniform transfer integrals give a slightly larger separation between the energy states, though the increase is the least for ϵ_{ST} . Hence the change in transfer integrals does not affect the charge and spin-density distribution in a perceptible manner.

Our VB computations with exact solutions of the model Hamiltonian on the complexes **I**, **II** and **III** reveal that there is a general and linear increase in the absolute energy values for the states S_0 , S_1 , T_1 , T_2 and Q_1 and Q_2 as a function of $-K_{\text{OO}}$ but differing slopes for the variation of energies. Combining our earlier [15] and present reports it shows that the spin excitation gaps in all those dimeric complexes with the bridging moiety

Table 5
Energy in eV as a function of K_{OO} (eV) with the transfer integral Cu–O (1.30 eV) and Cu–N (1.50 eV) for complexes **II** and **III**

K_{OO}	II			III		
	ϵ_{SS}	ϵ_{TT}	ϵ_{QQ}	ϵ_{SS}	ϵ_{TT}	ϵ_{QQ}
0.0	0.8035	0.8033	0.0021	0.8056	0.8055	0.0001
-0.1	0.8122	0.7961	0.0041	0.8147	0.7980	0.0102
-0.2	0.8122	0.7961	0.0223	0.8251	0.7921	0.0222
-0.3	0.8329	0.7763	0.0365	0.8355	0.7851	0.0365
-0.4	0.8443	0.7630	0.0535	0.8472	0.7634	0.0422

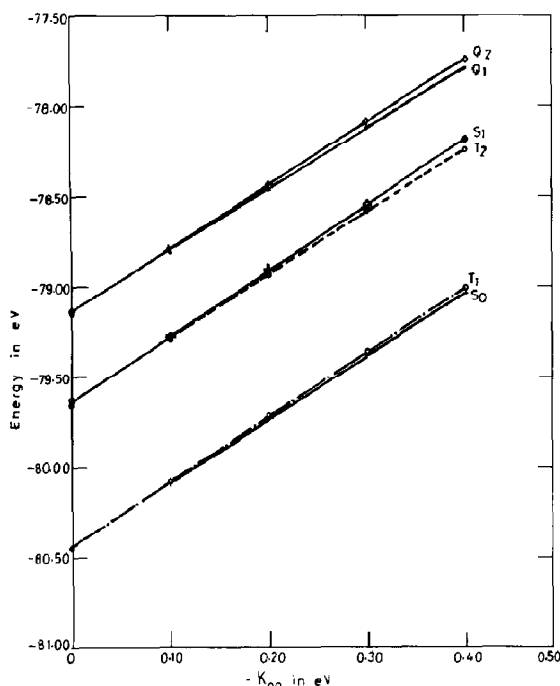
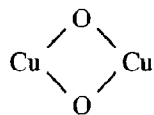


Fig. 2. Variation of different energies with K_{OO} for the complex I. S_0 and S_1 stand for ground- and first-excited singlet states. T_1 and T_2 represent first- and second-excited triplet states and Q_1 and Q_2 are the first- and second-excited quintet states.

Table 6

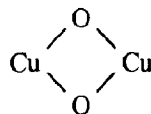
Energy gaps in eV for $K_{OO} = -0.4$ eV for complex II with (i) uniform transfer integral value for both Cu-O and Cu-N bonds set at 1.40 eV and (ii) non-uniform transfer integral values of Cu-N and Cu-O set at 1.30 and 1.50 eV, respectively

	(i)	(ii)
ϵ_{ST}	0.0256	0.0262
ϵ_{SQ}	1.2195	1.2388
ϵ_{SS}	0.8211	0.8443
ϵ_{TT}	0.7247	0.7630
ϵ_{QQ}	0.0486	0.0535



are almost entirely controlled by the exchange integral K_{OO} . However, the inclusion of a fifth coordination on the axial sites of copper(II) increases the excitation gaps which are slightly dependent on

the nature of the fifth atom. Predictions of ϵ_{ST} and ϵ_{SQ} for the nonaxial I are less than those for the axial II and III and are in general agreement with experimental results [16]. Generally the VB prediction of such excitation gaps compares reasonably with experimental results [16,31-35] and favourably with other methodologies [11,12]. As a general rule, the spin densities in $S=1$ states for various complexes with other than the



moiety do not change much but the changes in $S=2$ are different. The geometries of the complexes influence some parameters via changes in hybridisation of oxygen orbitals but they do not seem to affect the general ordering of spin states. The general applicability and extension of this calculation using the model Hamiltonian to other systems is restricted by the lack of parameters for atoms other than those considered here.

Acknowledgement

We thank Dr. S. Ramasesha, Indian Institute of Science, Bangalore for the computer program. One of us (PKM) is thankful to the Indian Institute of Technology, Madras for a fellowship. Thanks are also due to the Department of Science and Technology, New Delhi for funding the project to PTM (DST/RSIC/004/PTM).

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