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Original Scientific Paper

On the Magnetic Exchange Parameter for an O–Cu–Cu–O Component of Cu^{II} Carboxylate Dimers*

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Abstract. Two approximate formulae are derived for the magnetic exchange parameter, $J = ½\{E(\text{singlet}) - E(\text{triplet})\}$, for an O–Cu–Cu–O component of Cu^{II} carboxylate dimers. The derivations use standard valence bond and molecular orbital techniques, but the effects of superexchange are incorporated in different ways. A superexchange parameter k measures the extent of delocalization of oxygen lone-pair electrons into singly occupied $3d_{x^2-y^2}$ atomic orbitals of the Cu^{II} ions. The two formulae for J are equivalent only when $k = 0$ and $k = \infty$. The formulae are compared, and suggestions are made for elaborations of them. The roles of two types of "*cis* O–O overlap" for stabilizing (*via* covalent-ionic resonance) the antiferromagnetic spin state are re-stated for 10-electron 6-centre (with two carboxylate ligands) as well as the 6-electron 4-centre bonding units.

Keywords: copper carboxylate dimer, antiferromagnetism, magnetic exchange parameter, superexchange, "*cis* O–O overlap"

INTRODUCTION

Six-electron 4-centre bonding units, *i.e.* six electrons distributed amongst four overlapping atomic orbitals (AOs) located around four atomic centres (**A**, **B**, **C** and **D**), occur in many molecular systems.[1] This type of bonding unit is present in each $Cu^{II}(RCOO^-)Cu^{II}$ component of the antiferromagnetic copper carboxylate dimer, $Cu_2(RCOO)_4 \cdot L_2$[2–4] for which **A** and **D** are the oxygen atoms, and **B** and **C** are the Cu^{II} ions. The relevant AOs for two carboxylate ligands, which are associated with a 10-electron 6-centre bonding unit, and the Cu^{II} ions are displayed in Figure 1.

Estimates of values of the magnetic exchange parameter for copper carboxylate dimers ($J = ½(^1E - {}^3E)$) range from −50 to $-250\ \text{cm}^{-1}$.[6] The origin of the antiferromagnetism has been associated with "*cis* O–O overlap" *via* covalent-ionic resonance,[2–4] which comes into effect when superexchange occurs.

In this paper, we derive and compare two approximate formulae for the magnetic exchange parameter J, which are obtained from valence bond (VB)[2(e)] and 4-centre molecular orbital (MO)[2(b)] theory. (These formulae are those of Eqs. (17) and (18) below.) It is also shown how the VB expression for J can be modified for a 10-electron 6-centre bonding unit, so that the four oxygen atoms of two carboxylate ligands are included. It is not the intention to provide a theoretical estimate of the magnitude of J. Rather it is primarily to provide

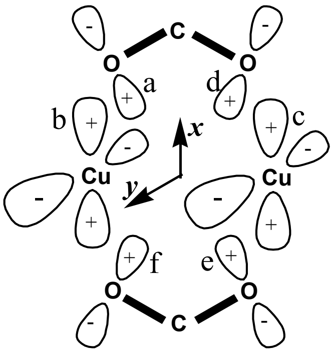

Figure 1. Overlapping oxygen AOs (a,d,e and f – displayed here as 2pπ′ AOs) and copper (b and c) AOs for two carboxylate ligands and two Cu^{II} $3d_{x^2-y^2}$ AOs. Lateral overlap of the $3d_{x^2-y^2}$ AOs generates a Cu–Cu δ bond.[5] The a, d, e and f AOs overlap with the positive lobes of the b and c AOs. For convenience throughout the text, linear VB structures are used for $O-Cu^{II}-Cu^{II}-O$, with **A** and **D** = **O**, and **B** and **C** = **Cu**. Atomic formal charges have been omitted from these structures.

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* Dedicated to Professor Zvonimir Maksić on the occasion of his 70th birthday.

details of the derivation of Eq. (23) of ref. 2(e), and to focus further attention on types of "*cis* O–O overlap" contributions to the stabilization of the singlet spin state.

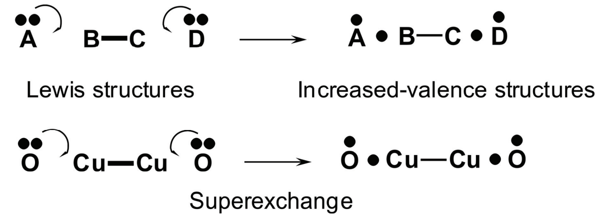
Throughout, zero differential overlap (ZDO) is assumed; the AO overlap integrals S_{ad}, S_{bc}, S_{ac} and S_{db} in particular for the Cu^{II} acetate dimer have small magnitudes (*cf.* Table 1).

The VB section of this paper initially utilizes an aspect of "increased-valence" theory for 6-electron 4-centre bonding units. Relevant details for this theory are described in the Appendix.

VALENCE BOND THEORY

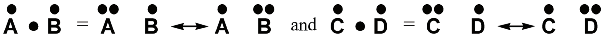
(I) Superexchange and VB Structures

For both VB and MO theory, the origin of the antiferromagnetism of Cu^{II} carboxylate dimers has been associated primarily with *"cis* O–O overlap" stabilization of the singlet-spin state.[2–4] This effect manifests itself *via* superexchange,

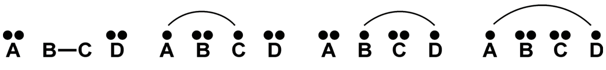


i.e. some delocalization of oxygen lone-pair electrons into the singly-occupied $3d_{x^2-y^2}$ AOs of the Cu^{II} ions, together with associated covalent-ionic resonance $(\mathbf{AB})(\mathbf{CD}) \leftrightarrow (\mathbf{AB})^-(\mathbf{CD})^+ \leftrightarrow (\mathbf{AB})^+(\mathbf{CD})^-$.

Using the Pauling "three-electron bond" identities, (see refs. 2–4 and the Appendix), it is easy to deduce



that the (covalent) singlet-spin "increased-valence" structure[1,2] is equivalent to resonance between the Lewis structures ^{1}**1**-^{1}**4**,



^{1}**1** ^{1}**2** ^{1}**3** ^{1}**4**

three of which (structures ^{1}**2**–^{1}**4**) are of the *Dewar/singlet-diradical/"long-bond*" type.[1–4] Four triplet-spin "covalent" Lewis structures have parallel spins for the two electrons that singly-occupy AOs.

^{3}**1** ^{3}**2** ^{3}**3** ^{3}**4**

Because the AO overlap integrals S_{bc}, $S_{ac} = S_{bd}$ and S_{ad} have small magnitudes, these two sets of four Lewis structures are essentially degenerate. They are stabilized to different extents by resonance with the ionic structures. There are six singlet-spin ionic structures (^{1}**5**-^{1}**10**),

Table 1. Atomic orbital overlap integrals

	pπ′ oxygen[4]	sp^2 hybridized oxygen[3]
$S_{ab} = S_{dc}$	0.06941	0.0692
$S_{ac} = S_{db}$	0.00038	0.00053
S_{ad}	0.01960	0.01127
S_{bc}	0.00109	0.00023

^{1}**5** ^{1}**6**

^{1}**7** ^{1}**8**

^{1}**9** ^{1}**10**

and two triplet-spin ionic structures (^{3}**7** and ^{3}**8**).

^{3}**7** ^{3}**8**

The formula for J reported in ref. 2(e), was deduced by assuming that the primary stabilizations of the singlet Lewis structures ^{1}**1**, ^{1}**2** ↔ ^{1}**3** and ^{1}**4** occur *via* ^{1}**1** ↔ ^{1}**5** ↔ ^{1}**6**, ^{1}**2** ↔ ^{1}**3** ↔ ^{1}**7** ↔ ^{1}**8**, and ^{1}**4** ↔ ^{1}**9** ↔ ^{1}**10** covalent ionic resonances, respectively. The primary covalent-ionic stabilization for the triplet spin-state was assumed to occur *via* the ^{3}**2** ↔ ^{3}**3** ↔ ^{3}**7** ↔ ^{3}**8** resonance. For each spin state, the covalent-ionic resonances **1** ↔ **7** ↔ **8** and **4** ↔ **7** ↔ **8** were ignored, as were ^{1}**2** ↔ ^{1}**3** ↔ ^{1}**5** ↔ ^{1}**6** and ^{1}**2** ↔ ^{1}**3** ↔ ^{1}**9** ↔ ^{1}**10** for the singlet spin state. The effect of their inclusion will be described later in this paper.

(II) Wavefunctions for VB Structures

For the ($S = M_S = 0$) singlet spin-state, the wavefunction for the covalent increased-valence structure (see Appendix) is given by Eqs. (1)–(3)

$$^1\Psi(\mathrm{cov}) = \left(\begin{array}{l} \left|\mathrm{a}^\alpha (\mathrm{a}+k\mathrm{b})^\beta \mathrm{b}^\alpha \mathrm{c}^\beta (k\mathrm{c}+\mathrm{d})^\alpha \mathrm{d}^\beta\right| + \\ \left|\mathrm{d}^\alpha (\mathrm{d}+k\mathrm{c})^\beta \mathrm{c}^\alpha \mathrm{b}^\beta (k\mathrm{b}+\mathrm{a})^\alpha \mathrm{a}^\beta\right| \end{array} \right) \Big/ \left\{2^{1/2}\left(k^2+1\right)\right\} \tag{1}$$

$$= \left\{ \begin{array}{l} \left(\left|\mathrm{a}^\alpha\mathrm{a}^\beta\mathrm{b}^\alpha\mathrm{c}^\beta\mathrm{d}^\alpha\mathrm{d}^\beta\right| + \left|\mathrm{d}^\alpha\mathrm{d}^\beta\mathrm{c}^\alpha\mathrm{b}^\beta\mathrm{a}^\alpha\mathrm{a}^\beta\right|\right)/2^{1/2} + \\ k\left(\left|\mathrm{a}^\alpha\mathrm{b}^\beta\mathrm{b}^\alpha\mathrm{c}^\beta\mathrm{d}^\alpha\mathrm{d}^\beta\right| + \left|\mathrm{d}^\alpha\mathrm{d}^\beta\mathrm{c}^\alpha\mathrm{b}^\beta\mathrm{b}^\alpha\mathrm{a}^\beta\right|\right)/2^{1/2} + \\ k\left(\left|\mathrm{a}^\alpha\mathrm{a}^\beta\mathrm{b}^\alpha\mathrm{c}^\beta\mathrm{c}^\alpha\mathrm{d}^\beta\right| + \left|\mathrm{d}^\alpha\mathrm{c}^\beta\mathrm{c}^\alpha\mathrm{b}^\beta\mathrm{a}^\alpha\mathrm{a}^\beta\right|\right)/2^{1/2} + \\ k^2\left(\left|\mathrm{a}^\alpha\mathrm{b}^\beta\mathrm{b}^\alpha\mathrm{c}^\beta\mathrm{c}^\alpha\mathrm{d}^\beta\right| + \left|\mathrm{d}^\alpha\mathrm{c}^\beta\mathrm{c}^\alpha\mathrm{b}^\beta\mathrm{b}^\alpha\mathrm{a}^\beta\right|\right)/2^{1/2} \end{array} \right\} \Big/ \left(k^2+1\right) \tag{2}$$

$$\begin{aligned}{}^{1}\Psi(\mathrm{cov}) &= \left\{{}^{1}\Psi_{\mathbf{1}} + k\left({}^{1}\Psi_{\mathbf{2}} + {}^{1}\Psi_{\mathbf{3}}\right) + k^{2}\left({}^{1}\Psi_{\mathbf{4}}\right)\right\}\Big/\left(k^{2}+1\right) = \\ &\left\{{}^{1}\Psi_{\mathbf{1}} + 2^{1/2}k\left({}^{1}\Psi_{\mathbf{2+3}}\right) + k^{2}\left({}^{1}\Psi_{\mathbf{4}}\right)\right\}\Big/\left(k^{2}+1\right)\end{aligned} \tag{3}$$

In Eqs.(1)−(3), k is the superexchange parameter, which measures the extent of delocalization of the oxygen a and d electrons of Lewis structures ${}^{1}\mathbf{1}$ and ${}^{3}\mathbf{1}$ into the singly-occupied copper b and c AOs of these VB structures. For the same value of k, the ($S = 1$) triplet spin wavefunction (see Appendix) is given by Eq.(4).

$${}^{3}\Psi(\mathrm{cov}) = \left\{{}^{3}\Psi_{\mathbf{1}} + 2^{1/2}k\left({}^{3}\Psi_{\mathbf{2+3}}\right) + k^{2}\left({}^{3}\Psi_{\mathbf{4}}\right)\right\}\Big/\left(k^{2}+1\right) \tag{4}$$

Each of the ${}^{1}\Psi_{\mathbf{1}}$, ${}^{1}\Psi_{\mathbf{2+3}} = ({}^{1}\Psi_{\mathbf{2}} + {}^{1}\Psi_{\mathbf{3}})/2^{½}$, ${}^{1}\Psi_{\mathbf{4}}$, and ${}^{3}\Psi_{\mathbf{2+3}} = ({}^{3}\Psi_{\mathbf{2}} + {}^{3}\Psi_{\mathbf{3}})/2^{½}$, interacts with its ionic partner ${}^{1}\Psi_{\mathbf{5+6}}$, ${}^{1}\Psi_{\mathbf{7+8}}$, ${}^{1}\Psi_{\mathbf{9+10}}$, and ${}^{3}\Psi_{\mathbf{7+8}}$,

$$\begin{aligned}{}^{1}\Psi_{\mathbf{5+6}} &= \left({}^{1}\Psi_{\mathbf{5}} + {}^{1}\Psi_{\mathbf{6}}\right)\big/2^{1/2} = \\ &\left(\left|\mathrm{a}^{\alpha}\mathrm{a}^{\beta}\mathrm{b}^{\alpha}\mathrm{b}^{\beta}\mathrm{d}^{\alpha}\mathrm{d}^{\beta}\right| + \left|\mathrm{a}^{\alpha}\mathrm{a}^{\beta}\mathrm{c}^{\alpha}\mathrm{c}^{\beta}\mathrm{d}^{\alpha}\mathrm{d}^{\beta}\right|\right)\big/2^{1/2}\end{aligned} \tag{5}$$

$$\begin{aligned}{}^{1}\Psi_{\mathbf{7+8}} &= \left({}^{1}\Psi_{\mathbf{7}} + {}^{1}\Psi_{\mathbf{8}}\right)\big/2^{1/2} = \\ &\left(\begin{matrix}\left|\mathrm{a}^{\alpha}\mathrm{a}^{\beta}\mathrm{b}^{\alpha}\mathrm{b}^{\beta}\mathrm{c}^{\alpha}\mathrm{d}^{\beta}\right| + \left|\mathrm{a}^{\alpha}\mathrm{a}^{\beta}\mathrm{b}^{\alpha}\mathrm{b}^{\beta}\mathrm{d}^{\alpha}\mathrm{c}^{\beta}\right| + \\ + \left|\mathrm{d}^{\alpha}\mathrm{d}^{\beta}\mathrm{c}^{\alpha}\mathrm{c}^{\beta}\mathrm{b}^{\alpha}\mathrm{a}^{\beta}\right| + \left|\mathrm{d}^{\alpha}\mathrm{d}^{\beta}\mathrm{c}^{\alpha}\mathrm{c}^{\beta}\mathrm{a}^{\alpha}\mathrm{b}^{\beta}\right|\end{matrix}\right)\Bigg/2\end{aligned} \tag{6}$$

$$\begin{aligned}{}^{1}\Psi_{\mathbf{9+10}} &= \left({}^{1}\Psi_{\mathbf{9}} + {}^{1}\Psi_{\mathbf{10}}\right)\big/2^{1/2} = \\ &\left(\left|\mathrm{a}^{\alpha}\mathrm{a}^{\beta}\mathrm{b}^{\alpha}\mathrm{b}^{\beta}\mathrm{c}^{\alpha}\mathrm{c}^{\beta}\right| + \left|\mathrm{b}^{\alpha}\mathrm{b}^{\beta}\mathrm{c}^{\alpha}\mathrm{c}^{\beta}\mathrm{d}^{\alpha}\mathrm{d}^{\beta}\right|\right)\big/2^{1/2}\end{aligned} \tag{7}$$

$$\begin{aligned}{}^{3}\Psi_{\mathbf{7-8}} &= \left({}^{3}\Psi_{\mathbf{7}} + {}^{3}\Psi_{\mathbf{8}}\right)\big/2^{1/2} = \\ &\left(\begin{matrix}\left|\mathrm{a}^{\alpha}\mathrm{a}^{\beta}\mathrm{b}^{\alpha}\mathrm{b}^{\beta}\mathrm{c}^{\alpha}\mathrm{d}^{\beta}\right| - \left|\mathrm{a}^{\alpha}\mathrm{a}^{\beta}\mathrm{b}^{\alpha}\mathrm{b}^{\beta}\mathrm{d}^{\alpha}\mathrm{c}^{\beta}\right| + \\ + \left|\mathrm{d}^{\alpha}\mathrm{d}^{\beta}\mathrm{c}^{\alpha}\mathrm{c}^{\beta}\mathrm{b}^{\alpha}\mathrm{a}^{\beta}\right| - \left|\mathrm{d}^{\alpha}\mathrm{d}^{\beta}\mathrm{c}^{\alpha}\mathrm{c}^{\beta}\mathrm{a}^{\alpha}\mathrm{b}^{\beta}\right|\end{matrix}\right)\Bigg/2\end{aligned} \tag{8}$$

With small λ_{i}^{2} omitted from the normalization constant we obtain Eqs. (9) and (10) as the wavefunctions for the resulting covalent-ionic resonance.

$${}^{1}\Psi \approx \left\{\begin{matrix}{}^{1}\Psi_{\mathbf{1}} + \lambda_{1}{}^{1}\Psi_{\mathbf{5+6}} + \\ 2^{1/2}k\left({}^{1}\Psi_{\mathbf{2+3}} + {}^{1}\lambda_{2}{}^{1}\Psi_{\mathbf{7+8}}\right) + \\ k^{2}\left({}^{1}\Psi_{\mathbf{4}} + {}^{1}\lambda_{4}{}^{1}\Psi_{\mathbf{9+10}}\right)\end{matrix}\right\}\Bigg/\left(k^{2}+1\right) \tag{9}$$

$${}^{3}\Psi \approx \left\{\begin{matrix}{}^{3}\Psi_{\mathbf{1}} + 2k^{1/2}\left({}^{3}\Psi_{\mathbf{2+3}} + {}^{3}\lambda_{2}{}^{3}\Psi_{\mathbf{7+8}}\right) + \\ k^{2}\left({}^{3}\Psi_{\mathbf{4}}\right)\end{matrix}\right\}\Bigg/\left(k^{2}+1\right) \tag{10}$$

(III) Stabilization *via* covalent-ionic resonance

In the discussion below, the $\beta^{\circ}{}_{\mu\nu}$ and $\gamma_{\mu\nu}$ are one-electron core resonance integrals, and two-electron repulsion integrals, respectively.

With ${}^{1}E_{\mathrm{i}}(\mathrm{cov}) \approx {}^{3}E_{\mathrm{i}}(\mathrm{cov}) = E_{\mathrm{i}}(\mathrm{cov})$ and $E(\Psi_{\mathbf{i}} + \lambda_{\mathrm{j}}\Psi_{\mathbf{j}}) \approx E(\Psi_{\mathbf{i}}) - \langle\Psi_{\mathbf{i}}|H|\Psi_{\mathbf{j}}\rangle^{2}/\{E(\Psi_{\mathbf{j}}) - E(\Psi_{\mathbf{i}})\}$ for small λ_{j}, we obtain Eqs. (11)−(14) for covalent-ionic resonance stabilizations.*

$$E\left({}^{1}\Psi_{\mathbf{1}} + {}^{1}\lambda_{1}{}^{1}\Psi_{\mathbf{5+6}}\right) \approx E_{\mathbf{1}}(\mathrm{cov}) - 4\left(\beta^{\circ}{}_{\mathrm{bc}}\right)^{2}\big/\left(\gamma_{\mathrm{bb}} - \gamma_{\mathrm{bc}}\right) \tag{11}$$

$$E\left({}^{1}\Psi_{\mathbf{4}} + {}^{1}\lambda_{4}{}^{1}\Psi_{\mathbf{9+10}}\right) \approx E_{\mathbf{4}}(\mathrm{cov}) - 4\left(\beta^{\circ}{}_{\mathrm{ad}}\right)^{2}\big/\left(\gamma_{\mathrm{aa}} - \gamma_{\mathrm{ad}}\right) \tag{12}$$

$$E\left({}^{1}\Psi_{\mathbf{2+3}} + {}^{1}\lambda_{2}{}^{1}\Psi_{\mathbf{7+8}}\right) \approx E_{\mathbf{2}}(\mathrm{cov}) - \frac{2\left(\beta^{\circ}{}_{\mathrm{ad}} + \beta^{\circ}{}_{\mathrm{bc}}\right)^{2}}{\left({}^{1}E_{7} - E_{2}\right)} \tag{13}$$

$$E\left({}^{3}\Psi_{\mathbf{2+3}} + {}^{3}\lambda_{2}{}^{3}\Psi_{\mathbf{7+8}}\right) \approx E_{\mathbf{2}}(\mathrm{cov}) - \frac{2\left(-\beta^{\circ}{}_{\mathrm{ad}} - \beta^{\circ}{}_{\mathrm{bc}}\right)^{2}}{\left({}^{3}E_{7} - E_{2}\right)} \tag{14}$$

With ${}^{3}A_{\mathbf{2,7}} = {}^{3}E_{\mathbf{7}} - E_{\mathbf{2}}$, $J_{\mathrm{ab}} = \langle\mathrm{a}(1)\mathrm{b}(2)|H(1,2)|\mathrm{b}(1)\mathrm{a}(2)\rangle$ and ${}^{1}E_{\mathbf{7}} = {}^{3}E_{\mathbf{7}} + 2J_{\mathrm{ab}}$, we obtain Eqs. (15) and (16).

$$E\left({}^{1}\Psi_{\mathbf{2+3}} + {}^{1}\lambda_{2}{}^{1}\Psi_{\mathbf{7+8}}\right) \approx E_{\mathbf{2}}(\mathrm{cov}) - \frac{2\left(\beta^{\circ}{}_{\mathrm{ad}} + \beta^{\circ}{}_{\mathrm{bc}}\right)^{2}}{\left({}^{3}A_{\mathbf{2,7}} + 2J_{\mathrm{ab}}\right)} \tag{15}$$

$$\approx E_{\mathbf{2}}(\mathrm{cov}) - 2\left\{\frac{\left(\beta^{\circ}{}_{\mathrm{ad}} + \beta^{\circ}{}_{\mathrm{bc}}\right)^{2}}{{}^{3}A_{\mathbf{2,7}}}\right\}\left(1 - 2J_{\mathrm{ab}}\big/{}^{3}\mathrm{A}_{2,7}\right) \tag{16}$$

Using Eqs. (9)−(16), we obtain Eq. (17)

$$\begin{aligned}J &= ½\left({}^{1}E - {}^{3}E\right) = \\ &-2\left\{\begin{matrix}\dfrac{\left(\beta^{\circ}{}_{\mathrm{bc}}\right)^{2}}{\gamma_{\mathrm{bb}} - \gamma_{\mathrm{bc}}} - k^{2}\dfrac{\left(\beta^{\circ}{}_{\mathrm{ad}} + \beta^{\circ}{}_{\mathrm{bc}}\right)^{2}J_{\mathrm{ab}}}{\left(\gamma_{\mathrm{ab}} - \gamma_{\mathrm{ac}}\right)^{2}} + \\ k^{4}\dfrac{\left(\beta^{\circ}{}_{\mathrm{ad}}\right)^{2}}{\left(\gamma_{\mathrm{aa}} - \gamma_{\mathrm{ad}}\right)}\end{matrix}\right\}\Bigg/\left(k^{2}+1\right)^{2}\end{aligned} \tag{17}$$

as the resulting expression for the magnetic exchange parameter, *i.e*. Eq. (23) of ref. 2(e). In the present treatment, with AO overlap integrals omitted from normalization constants, J_{ab} is equal to $2S_{\mathrm{ab}}\beta^{\circ}{}_{\mathrm{ab}}$ + $\langle\mathrm{a}(1)\mathrm{b}(2)|1/r_{12}|\mathrm{b}(1)\mathrm{a}(2)\rangle$, which approximates to $2S_{\mathrm{ab}}\beta^{\circ}{}_{\mathrm{ab}}$ when ZDO is invoked. Because the overlap integrals S_{ab} and S_{cd} have magnitudes that are substantially larger than those of the other AO overlap integrals, $2S_{\mathrm{ab}}\beta^{\circ}{}_{\mathrm{ab}}$ is retained here.

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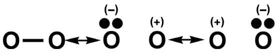
*When ZDO is assumed, $E(\Psi_{\mathbf{5+6}}) - E(\Psi_{\mathbf{1}})$ for Eq. (11) is equivalent to $E\{(|\mathrm{b}^{\alpha}\mathrm{b}^{\beta}| + |\mathrm{c}^{\alpha}\mathrm{c}^{\beta}|)/2^{½}\} - E\{(|\mathrm{b}^{\alpha}\mathrm{c}^{\beta}| + |\mathrm{c}^{\alpha}\mathrm{b}^{\beta}|)/2^{½}\}$, to give $\gamma_{\mathrm{bb}} - \gamma_{\mathrm{bc}}$. Similarly, $E(\Psi_{\mathbf{9+10}}) - E(\Psi_{\mathbf{4}})$ for Eq. (12) is equivalent to $E\{(|\mathrm{a}^{\alpha}\mathrm{a}^{\beta}| + |\mathrm{d}^{\alpha}\mathrm{d}^{\beta}|)/2^{½}\} - E\{(|\mathrm{a}^{\alpha}\mathrm{d}^{\beta}| + |\mathrm{d}^{\alpha}\mathrm{a}^{\beta}|)/2^{½}\}$, to give $\gamma_{\mathrm{aa}} - \gamma_{\mathrm{ad}}$. Also, $\langle\Psi_{\mathbf{5+6}}|H|\Psi_{\mathbf{1}}\rangle = 2\beta^{\circ}{}_{\mathrm{bc}}$ and $\langle\Psi_{\mathbf{9+10}}|H|\Psi_{\mathbf{4}}\rangle = 2\beta^{\circ}{}_{\mathrm{ad}}$.

(IV) *Cis* O−O Overlap Stabilization of the Singlet Spin State

As discussed in refs. 2−4, two types of covalent-ionic resonance produce *cis* O−O overlap stabilization of the singlet spin state.

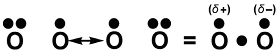
(a) Electron-pair bond covalent-ionic resonance,



$$\mathrm{O{-}O} \leftrightarrow \overset{(-)}{\ddot{\mathrm{O}}}\ \overset{(+)}{\mathrm{O}} \leftrightarrow \overset{(+)}{\mathrm{O}}\ \overset{(-)}{\ddot{\mathrm{O}}}$$

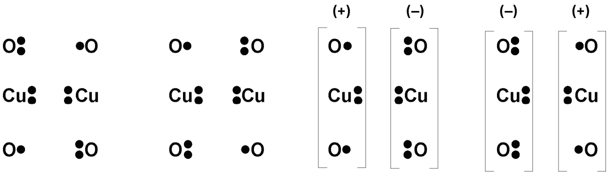
as exemplified by $^{1}\mathbf{4} \leftrightarrow {}^{1}\mathbf{9} \leftrightarrow {}^{1}\mathbf{10}$.

(b)(i) Pauling "three-electron bond" covalent-ionic resonance such as



$$\ddot{\mathrm{O}}\ \dot{\mathrm{O}} \leftrightarrow \dot{\mathrm{O}}\ \ddot{\mathrm{O}} = \overset{(\delta+)}{\dot{\mathrm{O}}} \bullet \overset{(\delta-)}{\dot{\mathrm{O}}}$$

(ii) Pauling "three-electron bond" covalent-ionic resonance, as exemplified by **11** ↔ **12** ↔ **13** ↔ **14**.



11 **12** **13** **14**

(V) 10-Electron 6-Centre Bonding

A 10-electron 6-centre bonding unit arises when consideration is given to the inclusion of a second carboxylate ligand. It introduces Lewis VB structures of types **11-14** for each spin state. Resonance between these types of VB structures generates type b(ii) O−O Pauling "three-electron bonds", and replaces (a) in importance.[2−4]

The VB formulation of J for 6-electron 4-centre bonding can be reformulated to accommodate 10-electron 6-centre bonding. This can be done by replacing the a and d AOs in Eqs. (1)−(17) with the MOs $\phi_{\mathrm{af}} = (\mathrm{a} + \mathrm{f})/2^{1/2}$, $\phi^{*}_{\mathrm{af}} = (\mathrm{a} - \mathrm{f})/2^{1/2}$ and $\phi_{\mathrm{de}} = (\mathrm{d} + \mathrm{e})/2^{1/2}$, $\phi^{*}_{\mathrm{de}} = (\mathrm{d} - \mathrm{e})/2^{1/2}$, in which e and f are the oxygen AOs for the second carboxylate ligand (*cf.* Figure 1). There are then two interacting $^{1}\Psi(\mathrm{cov})$ configurations: $^{1}\Psi_{\mathrm{I}}(\mathrm{cov}) = {}^{1}\Psi_{\mathrm{I}}(\phi_{\mathrm{af}},\mathrm{b},\mathrm{c},\phi_{\mathrm{de}})$ and $^{1}\Psi_{\mathrm{II}}(\mathrm{cov}) = {}^{1}\Psi_{\mathrm{II}}(\phi^{*}_{\mathrm{af}},\mathrm{b},\mathrm{c},\phi^{*}_{\mathrm{de}})$, and two interacting $^{3}\Psi(\mathrm{cov})$ configurations: $^{3}\Psi_{\mathrm{I}}(\mathrm{cov}) = {}^{3}\Psi_{\mathrm{I}}(\phi_{\mathrm{af}},\mathrm{b},\mathrm{c},\phi_{\mathrm{de}})$ and $^{3}\Psi_{\mathrm{II}}(\mathrm{cov}) = {}^{3}\Psi_{\mathrm{II}}(\phi^{*}_{\mathrm{af}},\mathrm{b},\mathrm{c},\phi^{*}_{\mathrm{de}})$. The four configurations are essentially degenerate, and the linear combinations $^{1}\Psi_{\mathrm{I}} + {}^{1}\Psi_{\mathrm{II}}$ and $^{3}\Psi_{\mathrm{I}} + {}^{3}\Psi_{\mathrm{II}}$ are also essentially degenerate, as are $^{1}\Psi_{\mathrm{I}} - {}^{1}\Psi_{\mathrm{II}}$ and $^{3}\Psi_{\mathrm{I}} - {}^{3}\Psi_{\mathrm{II}}$. Their degeneracy is removed *via* interaction with the linear combinations of ionic configurations, in which the a and d AOs are also replaced by the ϕ_{af}, ϕ^{*}_{af}, ϕ_{de} and ϕ^{*}_{de} MOs.

For small non-zero k, covalent-ionic resonance of the type (b)(i) is dominant for both 6-electron 4-centre and 10-electron 6-centre bonding units, whereas for large k, (a) is dominant for the 6-electron 4-centre bonding unit, and (b)(ii) is dominant for the 10-electron 6-centre bonding unit.

Extension of the theory so that four carboxylate ligands are accommodated involves the replacement of the a and d AOs by 4-centre oxygen MOs of the types (a ± f ± g ± i)/2 and (d ± e ± h ± j)/2.

4-CENTRE MOLECULAR ORBITAL THEORY

An earlier formula for the magnetic exchange parameter, Eq. (18),

$$J \approx -\left(\beta^{\circ}_{\mathrm{bc}} - 2k\beta^{\circ}_{\mathrm{ac}} + k^{2}\beta^{\circ}_{\mathrm{ad}}\right)^{2} \Big/ \left\{\left(k^{2}+1\right)^{2} K_{34}\right\} \tag{18}$$

was deduced from 4-centre MO theory[2(a),2(b)] (see also refs. 7 and 8). Here we repeat the derivation using a procedure that relates the 4-centre MO configurations to the Ψ(cov) and Ψ(ion) wavefunctions.

Initially, the four delocalized MOs of Eq. (19) are constructed,

$$\begin{aligned}
\phi_1 &= \{\mathrm{a} + \mathrm{d} + \lambda(\mathrm{b} + \mathrm{c})\}/(2 + 2\lambda^{2})^{1/2}\\
\phi_2 &= \{\mathrm{a} - \mathrm{d} + \mu(\mathrm{b} - \mathrm{c})\}/(2 + 2\mu^{2})^{1/2}\\
\phi_3 &= \{\lambda(\mathrm{a} + \mathrm{d}) - (\mathrm{b} + \mathrm{c})\}/(2 + 2\lambda^{2})^{1/2}\\
\phi_4 &= \{\mu(\mathrm{a} - \mathrm{d}) - (\mathrm{b} - \mathrm{c})\}/(2 + 2\mu^{2})^{1/2}
\end{aligned} \tag{19}$$

Because each of the AO overlap integrals has a small magnitude, both of the parameters λ and μ are assigned a value of k.

The singlet-spin wavefunction is given by Eq. (20)[2(a),2(b)]; see also refs. 7 and 8,

$$\begin{aligned}
{}^{1}\Psi &= {}^{1}\Phi_1 + \rho\,{}^{1}\Phi_2 = \\
&|\phi_1^{\alpha}\phi_1^{\beta}\phi_2^{\alpha}\phi_2^{\beta}\phi_3^{\alpha}\phi_3^{\beta}| + \rho|\phi_1^{\alpha}\phi_1^{\beta}\phi_2^{\alpha}\phi_2^{\beta}\phi_4^{\alpha}\phi_4^{\beta}|
\end{aligned} \tag{20}$$

which can be transformed *via* unitary transformations (*cf.* refs. 2(c), 2(d) and 9) to give Eq. (21).

$${}^{1}\Psi = (1-\rho)\,{}^{1}\Psi(\mathrm{cov}) + (1+\rho)\,{}^{1}\Psi(\mathrm{ion}) \tag{21}$$

The ($S = M_S = 1$) triplet-spin wavefunction is given by Eq. (22).

$${}^{3}\Psi = {}^{3}\Phi_1 = |\phi_1^{\alpha}\phi_1^{\beta}\phi_2^{\alpha}\phi_2^{\beta}\phi_3^{\alpha}\phi_4^{\alpha}| \tag{22}$$

Similar types of unitary transformations of this wavefunction give

$$^{3}\Psi = |a^{\alpha}\phi_1{}^{\beta}b^{\alpha}\phi_2{}^{\beta}c^{\alpha}d^{\alpha}| = |a^{\alpha}(a + kb)^{\beta}b^{\alpha}(d + kc)^{\beta}c^{\alpha}d^{\alpha}| = {}^{3}\Psi(\mathrm{cov}) \tag{23}$$

Because the AO overlap integrals have been omitted, the $^{3}\Psi$(cov) and $^{1}\Psi$(cov) are essentially degenerate. The stabilization of the $^{1}\Psi$ relative to $^{3}\Psi$ then arises from the covalent-ionic resonance *via* Eq. (24) for small λ.

$$\begin{aligned} &E\left\{{}^{1}\Psi(\mathrm{cov}) + \lambda\,{}^{1}\Psi(\mathrm{ion})\right\} \approx \\ &E\left\{{}^{1}\Psi(\mathrm{cov})\right\} - \frac{\left\langle {}^{1}\Psi(\mathrm{cov})\middle|H\middle|{}^{1}\Psi(\mathrm{ion})\right\rangle^{2}}{\left[E\left\{{}^{1}\Psi(\mathrm{ion})\right\} - E\left\{{}^{1}\Psi(\mathrm{cov})\right\}\right]} \end{aligned} \tag{24}$$

One approach to the calculation of this stabilization involves expressing the $^{1}\Psi$(cov) and $^{1}\Psi$(ion) in terms of the MO configuration $^{1}\Phi_1$ and $^{1}\Phi_2$, according to Eq. (25).

$$\begin{aligned} &{}^{1}\Psi(\mathrm{cov}) = \left({}^{1}\Phi_1 - {}^{1}\Phi_2\right)/2^{1/2}, \\ &{}^{1}\Psi(\mathrm{ion}) = \left({}^{1}\Phi_1 + {}^{1}\Phi_2\right)/2^{1/2} \end{aligned} \tag{25}$$

to give

$$\begin{aligned} &\left\langle {}^{1}\Psi(\mathrm{cov})\middle|H\middle|{}^{1}\Psi(\mathrm{ion})\right\rangle = \\ &\tfrac{1}{2}\left(\left\langle {}^{1}\Phi_1\middle|H\middle|{}^{1}\Phi_1\right\rangle - \left\langle {}^{1}\Phi_2\middle|H\middle|{}^{1}\Phi_2\right\rangle\right) = -\tfrac{1}{2}A = \\ &-\left(e_4 - e_3 - 2J_{34} + \tfrac{1}{2}J_{33} + \tfrac{1}{2}J_{44} + K_{34}\right)\text{[11]} \end{aligned} \tag{26}$$

$$e_4 = \left\{k^2\left(F_{\mathrm{aa}} - F_{\mathrm{ad}}\right) + F_{\mathrm{bb}} - F_{\mathrm{bc}} - 2k\left(F_{\mathrm{ab}} - F_{\mathrm{ac}}\right)\right\}/\left(k^2+1\right) \tag{27}$$

$$e_3 = \left\{k^2\left(F_{\mathrm{aa}} + F_{\mathrm{ad}}\right) + F_{\mathrm{bb}} + F_{\mathrm{bc}} - 2k\left(F_{\mathrm{ab}} + F_{\mathrm{ac}}\right)\right\}/\left(k^2+1\right) \tag{28}$$

$$e_4 - e_3 = 2\left(-k^2F_{\mathrm{ad}} - F_{\mathrm{bc}} + 2kF_{\mathrm{ac}}\right)/\left(k^2+1\right) \tag{29}$$

The ZDO expression for each of the (self-consistent field)[12] $F_{\mu\nu}$ of Eq. (29) is $F_{\mu\nu} = \beta°_{\mu\nu} - \frac{1}{2}P_{\mu\nu}\gamma_{\mu\nu}$, in which $P_{\mu\nu} = 2\Sigma C_{i\mu}C_{i\nu}$ (i = 1 to 3) is the μ–ν Coulson bond order calculated from the occupied MOs of the MO configuration $^{1}\Phi_1 = |\phi_1{}^{\alpha}\phi_1{}^{\beta}\phi_2{}^{\alpha}\phi_2{}^{\beta}\phi_3{}^{\alpha}\phi_3{}^{\beta}|$. The resulting expression for the F_{ad}, F_{bc} and $F_{\mathrm{ac}} = F_{\mathrm{db}}$, are those of Eq. (30).

$$\begin{aligned} &F_{\mathrm{ad}} = \beta°_{\mathrm{ad}} - \left\{\tfrac{1}{2}k^2/\left(k^2+1\right)\right\}\gamma_{\mathrm{ad}} \\ &F_{\mathrm{bc}} = \beta°_{\mathrm{bc}} - \left\{\tfrac{1}{2}/\left(k^2+1\right)\right\}\gamma_{\mathrm{bc}} \\ &F_{\mathrm{ac}} = F_{\mathrm{db}} = \beta°_{\mathrm{ac}} + \left\{\tfrac{1}{2}k/\left(k^2+1\right)\right\}\gamma_{\mathrm{ac}} \end{aligned} \tag{30}$$

We now can write

$$\begin{aligned} &e_4 - e_3 = 2\left(-k^2F_{\mathrm{ad}} - F_{\mathrm{bc}} + 2kF_{\mathrm{ac}}\right)/\left(k^2+1\right) = \\ &\left[\begin{aligned} &-2k^2\beta°_{\mathrm{ad}} - 2\beta°_{\mathrm{bc}} + \\ &4k\beta°_{\mathrm{ac}} + \left\{k^4/\left(k^2+1\right)\right\}\gamma_{\mathrm{ad}} + \\ &\left\{1/\left(k^2+1\right)\right\}\gamma_{\mathrm{bc}} + \left\{2k^2/\left(k^2+1\right)\right\}\gamma_{\mathrm{ac}} \end{aligned}\right] \Big/ \left(k^2+1\right) \end{aligned} \tag{31}$$

$$\begin{aligned} &J_{33} = J_{44} = J_{34} = \\ &\tfrac{1}{2}\left\{\begin{aligned} &k^4\left(\gamma_{\mathrm{aa}} + \gamma_{\mathrm{ad}}\right) + \gamma_{\mathrm{bb}} + \\ &\gamma_{\mathrm{bc}} + 2k^2\left(\gamma_{\mathrm{ab}} + \gamma_{\mathrm{ac}}\right) \end{aligned}\right\} \Big/ \left(k^2+1\right)^2 \end{aligned} \tag{32}$$

$$K_{34} = \tfrac{1}{2}\left\{\begin{aligned} &k^4\left(\gamma_{\mathrm{aa}} - \gamma_{\mathrm{ad}}\right) + \gamma_{\mathrm{bb}} - \\ &\gamma_{\mathrm{bc}} + 2k^2\left(\gamma_{\mathrm{ab}} - \gamma_{\mathrm{ac}}\right) \end{aligned}\right\} \Big/ \left(k^2+1\right)^2 \tag{33}$$

$$\begin{aligned} &\left\langle {}^{1}\Psi(\mathrm{cov})\middle|H\middle|{}^{1}\Psi(\mathrm{ion})\right\rangle = -\tfrac{1}{2}A = \\ &2\left(-k^2\beta°_{\mathrm{ad}} - \beta°_{\mathrm{bc}} + 2k\beta°_{\mathrm{ac}}\right)/\left(k^2+1\right) \end{aligned} \tag{34}$$

$$E\left\{{}^{1}\Psi(\mathrm{ion})\right\} - E\left\{{}^{1}\Psi(\mathrm{cov})\right\} = 2K_{34} \tag{35}$$

By substitution of Eqs. (34) and (35) into Eq. (36),

$$J = -\tfrac{1}{2}\frac{\left\langle {}^{1}\Psi(\mathrm{cov})\middle|H\middle|{}^{1}\Psi(\mathrm{ion})\right\rangle^{2}}{\left[E\left\{{}^{1}\Psi(\mathrm{ion})\right\} - E\left\{{}^{1}\Psi(\mathrm{cov})\right\}\right]} \tag{36}$$

we thereby obtain Eq. (18) for the magnetic exchange parameter.

For 10-electron 6-centre bonding, Eq. (37)[2(a)] gives the corresponding expression for *J*.

$$J = -\left\{\beta°_{\mathrm{bc}} - 8^{1/2}k\beta°_{\mathrm{ac}} + k^2\left(\beta°_{\mathrm{ad}} + \beta°_{\mathrm{af}}\right)^2\right\}\Big/\left\{\left(k^2+1\right)^2K_{56}\right\} \tag{37}$$

COMPARISONS AND IMPROVEMENTS TO EQUATIONS (17) AND (18)

(I) For $0 < k < \infty$, Eqs. (17) and (18) for J differ greatly, but are identical for each of $k = 0$ ($J = -2(\beta°_{\mathrm{bc}})^2/(\gamma_{\mathrm{bb}} - \gamma_{\mathrm{bc}})$) and $k = \infty$ ($J = -2(\beta°_{\mathrm{ad}})^2/(\gamma_{\mathrm{aa}} - \gamma_{\mathrm{ad}})$).

(II) When $k = 0$, no delocalization of the electrons occurs from the oxygen AOs a and d into the copper AOs b and c. The resulting VB structures are ^{1}**1**, ^{1}**5** and ^{1}**6**, and ^{3}**1**. When $k = \infty$, two electrons have delocalized from the doubly-occupied oxygen AOs a and d into the singly-occupied copper AOs b and c of the VB structures ^{1}**1** and ^{3}**1**. The resulting VB structures are ^{1}**4**, ^{1}**9** and $^1\mathbf{10}$, and $^3\mathbf{4}$. For these two sets of k values, the J of Eqs. (17) and (18) are equivalent, and the antiferromagnetism arises either from Cu−Cu electron-pair bond covalent-ionic resonance (k = 0) or from O−O electron-pair covalent ionic resonance ($k = \infty$).

(III) Because the magnitudes of S_{ad} and $S_{\mathrm{ab}} = S_{\mathrm{dc}}$ are substantially larger than the magnitudes of S_{bc} and $S_{\mathrm{ac}} = S_{\mathrm{db}}$, Eqs. (17) and (18) approximate to Eqs. (38) and (39), respectively

$$J = 2\left\{\begin{matrix} k^2\left(\beta^\circ{}_{\mathrm{ad}}\right)^2 J_{\mathrm{ab}}\Big/\left(\gamma_{\mathrm{ab}}-\gamma_{\mathrm{ac}}\right)^2 - \\ k^4\left(\beta^\circ{}_{\mathrm{ad}}\right)^2\Big/\left(\gamma_{\mathrm{aa}}-\gamma_{\mathrm{ad}}\right) \end{matrix}\right\}\Bigg/\left(k^2+1\right)^2 \tag{38}$$

$$J = -k^4\left(\beta^\circ{}_{\mathrm{ad}}\right)^2\Big/\left\{\left(k^2+1\right)^2 \mathrm{K}_{34}\right\} \tag{39}$$

Only Eq. (38) takes account of the stabilization of the singlet spin state *via* the $^1\mathbf{2} \leftrightarrow {}^1\mathbf{3} \leftrightarrow {}^1\mathbf{7} \leftrightarrow {}^1\mathbf{8}$ covalent-ionic resonance. It is "*cis* OO overlap" dependent *via* the $\beta^\circ_{\mathrm{ad}}$ core resonance integral, which is S_{ad} overlap dependent, as is the $^1\mathbf{4} \leftrightarrow {}^1\mathbf{9} \leftrightarrow {}^1\mathbf{10}$ stabilization.

(IV) For Eq. (17), terms that involve k and k^3 are introduced when for each spin state, allowance is made for the covalent-ionic resonances $^1\mathbf{2} \leftrightarrow {}^1\mathbf{3} \leftrightarrow {}^1\mathbf{5} \leftrightarrow {}^1\mathbf{6}$ and $^1\mathbf{2} \leftrightarrow {}^1\mathbf{3} \leftrightarrow {}^1\mathbf{9} \leftrightarrow {}^1\mathbf{10}$ for the singlet spin state. The additional terms (ΔJ) that contribute to the J of Eq. (17) are those of Eq. (40).

$$\Delta J = -2\left\{\begin{matrix} k\left(\beta^\circ{}_{\mathrm{ac}}+\beta^\circ{}_{\mathrm{bd}}\right)^2\Big/\left({}^1E_{5+6}-E_{2+3}\right)+ \\ k^3\left(\beta^\circ{}_{\mathrm{ac}}+\beta^\circ{}_{\mathrm{bd}}\right)^2\Big/\left({}^1E_{9+10}-E_{2+3}\right) \end{matrix}\right\}\Bigg/\left(k^2+1\right)^2 \tag{40}$$

Allowance for $\mathbf{1} \leftrightarrow \mathbf{7} \leftrightarrow \mathbf{8}$ and $\mathbf{4} \leftrightarrow \mathbf{7} \leftrightarrow \mathbf{8}$ covalent-ionic resonance for each spin state generates no net stabilization of the singlet spin state relative to the triplet spin state when the small exchange integrals $J_{\mathrm{ac}} \approx 2S_{\mathrm{ac}}\beta^\circ_{\mathrm{ac}}$ and $J_{\mathrm{db}} \approx 2S_{\mathrm{db}}\beta^\circ_{\mathrm{db}}$ are omitted from the relevant $^1E(\mathrm{ion}) - {}^1E(\mathrm{cov})$ terms.

(V) Eq. (36) involves no covalent-ionic resonance for the triplet spin state. This can be incorporated *via* inclusion of the MO configuration $^3\Phi_2$ (with for convenience, $S = M_S = 1$ here)

$$^3\Phi_2 = |\phi_2{}^\alpha\phi_2{}^\beta\phi_3{}^\alpha\phi_3{}^\beta\phi_1{}^\alpha\phi_4{}^\alpha| \tag{41}$$

$$= |\mathrm{a}^\alpha\phi_2{}^\beta\mathrm{b}^\alpha\phi_3{}^\beta\mathrm{c}^\alpha\mathrm{d}^\alpha| = 2k({}^3\Psi_{\mathbf{1}} - {}^3\Psi_{\mathbf{4}}) - (k^2-1)({}^3\Psi_{\mathbf{2}} + {}^3\Psi_{\mathbf{3}}) - (k^2+1)({}^3\Psi_{\mathbf{7}} + {}^3\Psi_{\mathbf{8}}) \tag{42}$$

as well as the $^3\Phi_1$ of Eq. (22) to construct the $^3\Psi$ wavefunction.

(VI) To conclude, it is noted that each of the $\langle\Psi(\mathrm{cov})|H|\Psi(\mathrm{ion})\rangle$ integrals is an example of a hopping integral,[13] and each of the E(ion) − E(cov) is an on-site coulomb repulsion integral.[13] Calzado and co-workers[13] give consideration to type (a) hopping integrals.

APPENDIX

Increased-valence theory for 6-electron 4-centre bonding units is described in detail in refs. 2(c), 2(d) and 9. In these references, it is deduced that Eq. (1) is equivalent to Eq. (A1),

$$^1\Psi(\mathrm{cov}) = \left(\begin{matrix} \left|\psi_{\mathrm{ab}}{}^\alpha\psi_{\mathrm{ab}}{}^\beta\psi^*{}_{\mathrm{ab}}{}^\alpha\,\psi^*{}_{\mathrm{dc}}{}^\beta\,\psi_{\mathrm{dc}}{}^\alpha\psi_{\mathrm{dc}}{}^\beta\right| + \\ \left|\psi_{\mathrm{dc}}{}^\alpha\psi_{\mathrm{dc}}{}^\beta\psi^*{}_{\mathrm{dc}}{}^\alpha\,\psi^*{}_{\mathrm{ab}}{}^\beta\,\psi_{\mathrm{ab}}{}^\alpha\psi_{\mathrm{ab}}{}^\beta\right| \end{matrix}\right)\Bigg/2^{1/2} \tag{A1}$$

in which $\psi_{\mathrm{ab}} = N(\mathrm{a} + k\mathrm{b})$, $\psi^*_{\mathrm{ab}} = N^*(k^*\mathrm{a} - \mathrm{b})$, $\psi_{\mathrm{dc}} = N(\mathrm{d} + k\mathrm{c})$, $\psi^*_{\mathrm{dc}} = N^*(k^*\mathrm{d} - \mathrm{c})$, with $k^* = k$ and $N = N^* = (k^2+1)^{-1/2}$ when AO overlap integrals are omitted. Similarly the (S =1, M_S = 0) triplet-spin $^3\Psi$(cov) can be expressed according to Eqs. (A2)−(A4).

$$^3\Psi(\mathrm{cov}) = \left(\begin{matrix} \left|\psi_{\mathrm{ab}}{}^\alpha\psi_{\mathrm{ab}}{}^\beta\psi^*{}_{\mathrm{ab}}{}^\alpha\,\psi^*{}_{\mathrm{dc}}{}^\beta\,\psi_{\mathrm{dc}}{}^\alpha\psi_{\mathrm{dc}}{}^\beta\right| - \\ \left|\psi_{\mathrm{dc}}{}^\alpha\psi_{\mathrm{dc}}{}^\beta\psi^*{}_{\mathrm{dc}}{}^\alpha\,\psi^*{}_{\mathrm{ab}}{}^\beta\,\psi_{\mathrm{ab}}{}^\alpha\psi_{\mathrm{ab}}{}^\beta\right| \end{matrix}\right)\Bigg/2^{1/2} \tag{A2}$$

$$= \left(\begin{matrix} \left|\mathrm{a}^\alpha(\mathrm{a}+k\mathrm{b})^\beta\mathrm{b}^\alpha\mathrm{c}^\beta(k\mathrm{c}+\mathrm{d})^\alpha\mathrm{d}^\beta\right| - \\ \left|\mathrm{d}^\alpha(\mathrm{d}+k\mathrm{c})^\beta\mathrm{c}^\alpha\mathrm{b}^\beta(k\mathrm{b}+\mathrm{a})^\alpha\mathrm{a}^\beta\right| \end{matrix}\right)\Bigg/\left\{2^{1/2}\left(\mathrm{k}^2+1\right)\right\} \tag{A3}$$

$$= \left\{\begin{matrix} \left(\left|\mathrm{a}^\alpha\mathrm{a}^\beta\mathrm{b}^\alpha\mathrm{c}^\beta\mathrm{d}^\alpha\mathrm{d}^\beta\right| - \left|\mathrm{d}^\alpha\mathrm{d}^\beta\mathrm{c}^\alpha\mathrm{b}^\beta\mathrm{a}^\alpha\mathrm{a}^\beta\right|\right)\Big/2^{1/2} + \\ k\left(\left|\mathrm{a}^\alpha\mathrm{b}^\beta\mathrm{b}^\alpha\mathrm{c}^\beta\mathrm{d}^\alpha\mathrm{d}^\beta\right| - \left|\mathrm{d}^\alpha\mathrm{d}^\beta\mathrm{c}^\alpha\mathrm{b}^\beta\mathrm{b}^\alpha\mathrm{a}^\beta\right|\right)\Big/2^{1/2} + \\ k\left(\left|\mathrm{a}^\alpha\mathrm{a}^\beta\mathrm{b}^\alpha\mathrm{c}^\beta\mathrm{c}^\alpha\mathrm{d}^\beta\right| - \left|\mathrm{d}^\alpha\mathrm{c}^\beta\mathrm{c}^\alpha\mathrm{b}^\beta\mathrm{a}^\alpha\mathrm{a}^\beta\right|\right)\Big/2^{1/2} + \\ k^2\left(\left|\mathrm{a}^\alpha\mathrm{b}^\beta\mathrm{b}^\alpha\mathrm{c}^\beta\mathrm{c}^\alpha\mathrm{d}^\beta\right| - \left|\mathrm{d}^\alpha\mathrm{c}^\beta\mathrm{c}^\alpha\mathrm{b}^\beta\mathrm{b}^\alpha\mathrm{a}^\beta\right|\right)\Big/2^{1/2} \end{matrix}\right\}\Bigg/\left(\mathrm{k}^2+1\right) \tag{A4}$$

The $(\psi_{\mathrm{ab}})^2(\psi^*_{\mathrm{ab}})^1$ and $(\psi_{\mathrm{dc}})^2(\psi^*_{\mathrm{dc}})^1$ configurations that are present in Eqs. (A1) and (A2) are MO formulations of Pauling "three-electron bond" configurations. Unitary transformations of the type $|\psi_{\mathrm{ab}}{}^\alpha\psi^*{}_{\mathrm{ab}}{}^\alpha| = -|\mathrm{a}^\alpha\mathrm{b}^\alpha|$ for pairs of bonding and antibonding MOs give the identities $(\psi_{\mathrm{ab}})^2(\psi^*_{\mathrm{ab}})^1 = (\mathrm{a})^1(\psi_{\mathrm{ab}})^1(\mathrm{b})^1$ and $(\psi_{\mathrm{dc}})^2(\psi^*_{\mathrm{dc}})^1 = (\mathrm{d})^1(\psi_{\mathrm{dc}})^1(\mathrm{c})^1$. We can then write $(\mathrm{a})^1(\psi_{\mathrm{ab}})^1(\mathrm{b})^1 = \{(\mathrm{a})^2(\mathrm{b})^1 + k(\mathrm{a})^1(\mathrm{b})^2\}/(k^2+1)^{1/2}$ and $(\mathrm{d})^1(\psi_{\mathrm{dc}})^1(\mathrm{c})^1 = \{(\mathrm{d})^2(\mathrm{c})^1 + k(\mathrm{d})^1(\mathrm{c})^2\}/(k^2+1)^{1/2}$, respectively. These equivalences are used to generate Eqs. (1) and (2) from Eq. (A1), and Eqs. (A3) and (A4) from Eq. (A2).

In all increased-valence publications, the Green-Linnett VB symbolism[14] is used to represent the $(\mathrm{a})^1(\psi_{\mathrm{ab}})^1(\mathrm{b})^1$ and $(\mathrm{d})^1(\psi_{\mathrm{dc}})^1(\mathrm{c})^1$ configurations. See also ref. 15 for a summary of increased-valence theory for 6-electron 4-centre bonding units.

REFERENCES

1. R. D. Harcourt, *Inorg*. *Chem*. **46** (2007) 5773−5778 and refs. 4,6,7,8,10,12,13 and 16 therein.
2. (a) R. D. Harcourt, *Aust. J. Chem.* **27** (1974) 2065−2073; (b) R. D. Harcourt, in: J.-L. Calais, O. Goscinski, J. Linderberg, and Y. Öhrn (Eds.), *Methods and Structure of Quantum Science*, Plenum, New York, 1976, pp. 105−122. (A list of typing corrections is available from the author. They are not required for the reading of the present paper.); (c) R. D. Harcourt, in: *Qualitative Valence Bond Descriptions of Electron-Rich Molecules, Lecture Notes in Chemistry*, Springer, Berlin, vol. 30, 1982, Sections 10−2, 10−3. (A 2003 update is available from the author); (d) R. D. Harcourt, in: Z. B. Maksić, and W. J. Orville-Thomas (Eds.), *Pauling's Legacy Modern Modelling of the Chemical Bond,* Elsevier, 1999, pp. 449−480; (e) R. D. Harcourt, *Eur. J. Inorg. Chem.* (2000) 1901−1916.
3. R. D. Harcourt and G. E. Martin, *J. Chem. Soc. Faraday II* **73** (1977) 1−14.
4. R. D. Harcourt, F. L. Skrezenek, and R. G. A. R. Maclagan, *J. Am. Chem. Soc.* **108** (1986) 5403−5408.
5. B. N. Figgis and R. L. Martin, *J. Chem. Soc.* (1956) 3837−3846.
6. R. W. Jotham, S. F. A. Kettle, and J. A. Marks, *J. Chem. Soc. Dalton* (1972) 428−438. See also (a) refs. 3−7 of ref. 3 above, and (b) H. U. Güdel, A. Siebler, and A. Furer, *Inorg. Chem*. **18** (1979) 1021−1023.
7. P. J. Hay, J. C. Thibeault, and R. Hoffmann, *J. Am. Chem. Soc.* **97** (1975) 4884−4899.
8. I. G. Dance, *Inorg. Chim. Acta* **9** (1974) 77−82.
9. R. D. Harcourt, (a) *J. Am. Chem. Soc*. **102** (1980) 5195−5201. Corrections, *J. Am. Chem. Soc*. **103** (1981) 5623. The corresponding unitary transformations for 10-electron 6-centre bonding units are presented in ref. 10 below.
10. R. D. Harcourt, *Aust. J. Chem.* **32** (1979) 933−948 and refs. 8 and 11 therein.
11. J. N. Murrell and K. L. McEwen, *J. Chem. Phys*. **25** (1956) 1143−1149.
12. J. A. Pople, *Trans. Farad. Soc*. **49** (1953) 1375−1385.
13. (a) C. J. Calzado, J. Cabrero, J. P. Malrieu, and R. Caballol, *J. Chem. Phys.* **116** (2002) 2728−2747; (b) C. J. Calzado, J. Cabrero, J. P. Malrieu, and R. Caballol, *J. Chem. Phys.* **116** (2002) 3985−4000.
14. M. Green and J. W. Linnett, *J. Chem. Soc* (1960) 4959−4965.
15. R. D. Harcourt and T. M. Klapötke, *Trends Inorg. Chem*. **9** (2006) 11−21.

SAŽETAK

O parametru magnetske izmjene za O−Cu−Cu−O komponentu Cu^{II} karboksilat dimera

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Izvedene su dvije aproksimative formule za parametar magnetske izmjene, $J = ½\{E(\text{singlet}) - E(\text{triplet})\}$, za O−Cu−Cu−O komponentu Cu^{II} karboksilat dimera. Izvedenice koriste standardne tehnike valentne veze i molekulskih orbitala, ali je efekt superizmjene ugrađen na različite načine. Parametar superizmjene k mjeri doseg delokalizacije osamljenog para kisika u jednostruko popunjenu $3d_{x^2-y^2}$ atomsku orbitalu Cu^{II} iona. Dvije formule za J su ekvivalentne samo onda kada je $k = 0$ i $k = \infty$. Formule su uspoređene i dani su savjeti za njihovo elaboriranje. Uloga dva tipa "*cis* O−O prekrivanja" na stabilizaciju (preko kovalentno-ionske rezonancije) anti-ferromagnetsko spin stanja su razmatrana za slučaj 10-elektrona 6-centara (sa dva karboksilat liganda) i 6-elektrona 4-centra vezne jedinice.