Supplementary Material

The McClure and Weiss Models of Fe-O₂ Bonding for Oxyhemes, and the HbO₂ + NO Reaction

Richard D. Harcourt
School of Chemistry, The University of Melbourne, Victoria 3101 Australia.
e-mail: r.harcourt@unimelb.edu.au

(A) Heitler-London singlet spin-pairing schemes for Fe²⁺(S =1) + O₂(S = 1) → Fe²⁺O₂(S = 0)

With \( a = d_z² \), \( b = \pi^*_z \), \( c = d_{xz} \) and \( d = \pi^*_y \), (not to be confused with the \( a, b, c \) and \( d \) AOs of Appendix 2), there are two (Heitler-London-type) singlet spin-pairing schemes when these orbitals are singly-occupied.

(i) In terms of Slater determinants, \( a-b \) and \( c-d \) spin-pairings give the (non-normalized) \( S = 0 \) spin wavefunction \( \Psi_1 \) of eqs 1-3.

\[
\Psi_1 = \left| (a^αb^β + b^αa^β)(c^αd^β + d^αc^β) \right| 
\]

\[
= -|a^αc^βb^δd^δ| - |a^αb^δc^βd^δ| + |a^αc^βb^δd^δ| + |a^αb^δc^βd^δ| 
\]

\[
\equiv -\text{Fe}^{II}(S = 1, M_S = 1).O₂(S = -M_S = -1) - \text{Fe}^{II}(S = -M_S = 1).O₂(S = M_S = 1) \\
+ \frac{1}{2}\{(\text{Fe}^{II}(S = 1, M_S = 0).O₂(S = 1, M_S = 0) - \text{Fe}^{II}(S = M_S = 0).O₂(S = M_S = 0))\} 
\]

This is a wavefunction for increased-valence structure 2 of Fig. 2.

(ii) \( a-d \) and \( b-c \) spin-pairings give the (non-normalized) \( S = 0 \) spin wavefunction \( \Psi_2 \) of eqs 4-6.

\[
\Psi_2 = \left| (a^αd^β + d^αa^β)(b^αc^β + c^αb^β) \right| 
\]

\[
= -|a^αc^βb^δd^δ| - |a^αd^βc^δd^δ| + |a^αd^βb^δc^δ| + |a^αc^βd^δb^δ| 
\]

\[
\equiv -\frac{1}{2}\{(\text{Fe}^{II}(S = 1, M_S = 0).O₂(S = 1, M_S = 0) + \text{Fe}^{II}(S = M_S = 0).O₂(S = M_S = 0)) \}
\]

\[
+ \text{Fe}^{II}(S = -M_S = 1).O₂(S = M_S = 1) + \text{Fe}^{II}(S = M_S = 1).O₂(S = -M_S = 1) 
\]

Because the \( a \) and \( d \) orbitals are orthogonal, as are the \( b \) and \( c \) orbitals, no net Fe²⁺-O₂ bonding occurs via this wavefunction.

For finite separation between the heme and O₂, \( \Psi_1 \) and \( \Psi_2 \) interact to give \( \Psi = C_1\Psi_1 + C_2\Psi_2 \).

At infinite separation between the heme and the O₂, \( \Psi_1 \) and \( \Psi_2 \) are degenerate, and do not
interact. With \( C_1 = -C_2 \) for the ground-state \( \Psi \) and \( C_1 = +C_2 \), for the excited state \( \Psi^* \), we obtain eqs 7 and 8 for these states.

\[
\Psi = -2\text{Fe}^{II}(S = -M_S = 1).\text{O}_2(S = M_S = 1)
\]

\[
-2\text{Fe}^{II}(S = M_S = 1).\text{O}_2(S = -M_S = 1) + \text{Fe}^{II}(S = 1, M_S = 0).\text{O}_2(S = 1, M_S = 0)
\]

and \( \Psi^* = -\text{Fe}^{II}(S = M_S = 0).\text{O}_2(S = M_S = 0) \) (7)

On dissociation, the ground-state \( \Psi \) of eq 7 is therefore a linear combination of three types of \( S = 0 \) configurations, each of which involves \( S = 1 \) spin configurations for the \( \text{Fe}^{II} \) and the \( \text{O}_2 \) with different values for their \( M_S \) spin quantum numbers.

(B) Delocalizations into Antibonding MOs

As well as via \( 3 \rightarrow 2 \) (Fig. 2) and \( 8 \rightarrow 9 \) (Fig. 4), increased-valence structures 2 and 9 can also be obtained by delocalizing electrons from:

(i) \( \text{Fe}^{2-} \) into the antibonding \( \pi_\alpha^* \) and \( \pi_\beta^* \) MOs of \( \text{(O}_2)^{2+} \), as in \( \text{16} \rightarrow \text{2} \) (Fig S1, cf. [S1]).

(ii) \( \text{O}^{2-} \) into the antibonding \( \pi_\gamma^* \) and \( \pi_\delta^* \) MOs of \( \text{(FeO)}^{2+} \), as in \( \text{17} \rightarrow \text{9} \) (Fig S2)

Using the a and b AOs to construct the wavefunctions for an A-B electron-pair bond and an A-B
antibonding MO, regardless of how the wavefunction for an A-B electron-pair bond is constructed, the wavefunction for a Green-Linnett type VB structure \( \tilde{\psi} = \tilde{\psi} \) is obtained when an electron is delocalized from a third atom into the antibonding A-B MO [S2].

(C) Interaction of Fe\(^{II}\)-O\(_2\) with Distal Histidine.

When one of the \( p_x \) or \( p_z \) AOds on the terminal O\(_A\) oxygen atom of VB structure 2 for Fe\(^{II}\)-O\(_2\) overlaps with the N-H hydrogen AO of the distal histidine, a (weak H-O) 6-electron 5-centre bonding unit is established, as in structure 18 \( \rightarrow \) 19 (Fig. S3)

\[
\begin{array}{c}
\text{N-H} \quad \text{O} \quad \text{Fe} \\
\text{O} \quad \text{Fe} \\
18 \quad \rightarrow \quad 19
\end{array}
\]

Fig. S3 Construction of increased-valence structure for Fe\(^{II}\)-O\(_2\) interaction with distal histidine.

The weak NH • O interaction can supplement the electrostatic interaction that arises in the absence of this type of bonding unit. The more negatively-charged is the O\(_A\) oxygen atom, the greater will be strength of the NH • O interaction.

O\(_2\) VB structures of type F (Fig. 1) have been used to construct VB structures for spiral chain O\(_4\) polymers [S4].

References
S2. Harcourt RD (2011) J Phys Chem A 115: 6610-6616 (In eqs 2 and 4, delete the negative signs.) See also S3 for additional calculations.