Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Principal Interacting Spin Orbital: Understanding the fragment interactions in open-shell systems

Fu Kit Sheong, Jing-Xuan Zhang and Zhenyang Lin *

Supplementary Information

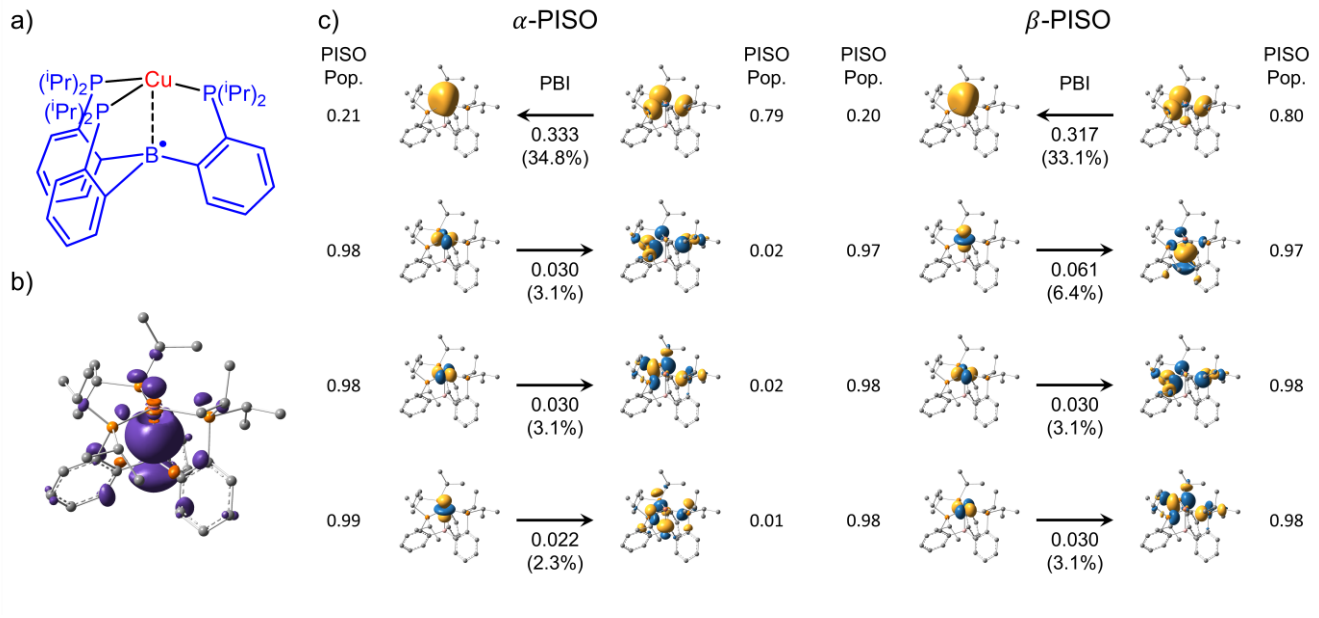

Figure S1 - PISO analysis of Cu(TPB). (a) Fragmentation scheme for the presented PISO analysis. (b) Spin density plot for the molecule, with purple indicating net α density and dark orange indicating net β density. (c) Dominant PISOs for the interaction between Cu centre and the TPB ligand. One can see that a very similar bonding pattern is seen in the first α-PISO pair and the first β-PISO pair, involving the donation of the lone pairs of three phosphine group to the Cu centre. The second and third α-PISO pairs are also quite similar to the third and fourth β-PISO pairs, showing the interactions between the two in-plane d orbitals of the metal centre and the phosphine groups. The second β-PISO involves the interaction between the metal d_{z2} orbital and the boron p orbital. For the fourth α-PISO pair, the PISO on the Cu side is still the d_{z2} orbital, but the PISO on the TPB side is quite different, similar to the VCl_4 case mentioned in the main text. This could again be attributed to the spin density present around the boron centre, as seen in panel (b). An isovalue of 0.05 $a_0^{-3/2}$ was adopted for the PISOs and 0.0025 $a_0^{-3/2}$ was adopted for the spin density. The presented PISO analysis is based on a B3LYP/6-311+G(d,p) single-point calculation adopting the atom coordinates presented in the original reference (*J. Am. Chem. Soc.* 2013, 135, 10, 3792-3795).

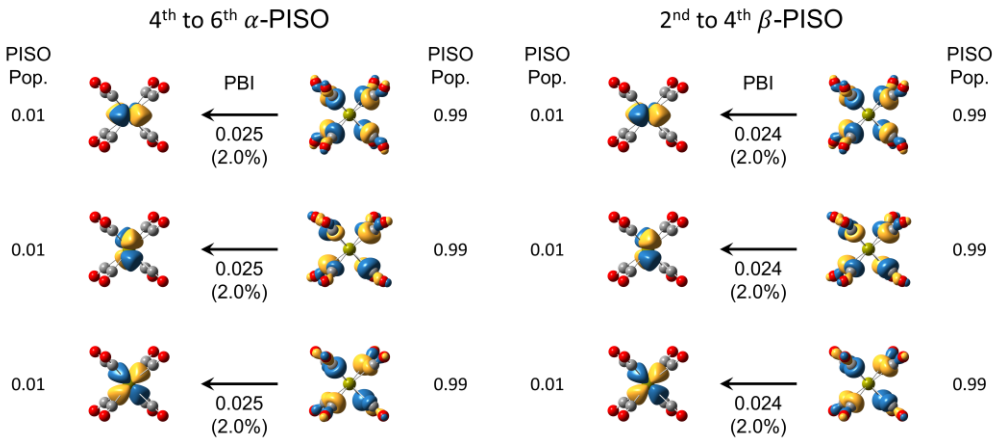

Figure S2 - PISO analysis of $Ca(CO)_8$. Note that the fourth to sixth α-PISO pairs are very similar to the second to fourth β-PISO pairs. An isovalue of 0.05 $a_0^{-3/2}$ was adopted for the PISOs.

Table S1: Comparison of PIO analysis result for $Ca(CO)_8$ with Calcium centre having two different basis sets

	Ca, C, O = def2-TZVP	Ca = def2-QZVP; C, O = def2-TZVP
1st α-PIO pair	0.205, 0.795, 0.326	0.212, 0.788, 0.334
2nd α-PIO pair	0.107, 0.893, 0.190	0.107, 0.893, 0.192
3rd α-PIO pair	0.107, 0.893, 0.190	0.107, 0.893, 0.192
1st β -PIO pair	0.198, 0.802, 0.317	0.204, 0.796, 0.325

Same geometry, only larger basis set

Result of Natural Resonance Theory (NRT) analysis

NRT of $Ca(CO)_8$

```
$NRTSTRA
   STR         ! Wgt =  9.95%
     LONE 1 1 2 2 3 1 4 1 5 1 6 1 7 1 8 1 9 1 10 1 11 1 12 1 13 1 14 1 15 1
          16 1 17 1 END
     BOND S 1 3 D 2 3 T 4 5 T 6 7 T 8 9 T 10 11 T 12 13 T 14 15 T 16 17 END
   END
   STR         ! Wgt =  9.95%
     LONE 1 1 2 1 3 1 4 2 5 1 6 1 7 1 8 1 9 1 10 1 11 1 12 1 13 1 14 1 15 1
          16 1 17 1 END
     BOND S 1 5 T 2 3 D 4 5 T 6 7 T 8 9 T 10 11 T 12 13 T 14 15 T 16 17 END
   END
   STR         ! Wgt =  9.95%
     LONE 1 1 2 1 3 1 4 1 5 1 6 2 7 1 8 1 9 1 10 1 11 1 12 1 13 1 14 1 15 1
          16 1 17 1 END
     BOND S 1 7 T 2 3 T 4 5 D 6 7 T 8 9 T 10 11 T 12 13 T 14 15 T 16 17 END
   END
   STR         ! Wgt =  9.95%
     LONE 1 1 2 1 3 1 4 1 5 1 6 1 7 1 8 2 9 1 10 1 11 1 12 1 13 1 14 1 15 1
          16 1 17 1 END
     BOND S 1 9 T 2 3 T 4 5 T 6 7 D 8 9 T 10 11 T 12 13 T 14 15 T 16 17 END
   END
   STR         ! Wgt =  9.95%
     LONE 1 1 2 1 3 1 4 1 5 1 6 1 7 1 8 1 9 1 10 2 11 1 12 1 13 1 14 1 15 1
          16 1 17 1 END
     BOND S 1 11 T 2 3 T 4 5 T 6 7 T 8 9 D 10 11 T 12 13 T 14 15 T 16 17 END
   END
   STR         ! Wgt =  9.95%
     LONE 1 1 2 1 3 1 4 1 5 1 6 1 7 1 8 1 9 1 10 1 11 1 12 2 13 1 14 1 15 1
          16 1 17 1 END
     BOND S 1 13 T 2 3 T 4 5 T 6 7 T 8 9 T 10 11 D 12 13 T 14 15 T 16 17 END
   END
   STR         ! Wgt =  9.95%
     LONE 1 1 2 1 3 1 4 1 5 1 6 1 7 1 8 1 9 1 10 1 11 1 12 1 13 1 14 2 15 1
          16 1 17 1 END
     BOND S 1 15 T 2 3 T 4 5 T 6 7 T 8 9 T 10 11 T 12 13 D 14 15 T 16 17 END
   END
   STR         ! Wgt =  9.95%
     LONE 1 1 2 1 3 1 4 1 5 1 6 1 7 1 8 1 9 1 10 1 11 1 12 1 13 1 14 1 15 1
          16 2 17 1 END
     BOND S 1 17 T 2 3 T 4 5 T 6 7 T 8 9 T 10 11 T 12 13 T 14 15 D 16 17 END
   END
   STR         ! Wgt =  1.75%
     LONE 1 2 3 1 4 1 5 1 6 1 7 2 8 1 9 1 10 1 11 1 12 1 13 1 14 1 15 1 16 1
          17 1 END
     BOND T 2 3 S 2 6 T 4 5 D 6 7 T 8 9 T 10 11 T 12 13 T 14 15 T 16 17 END
   END
   STR         ! Wgt =  1.75%
     LONE 1 2 2 1 3 1 5 1 6 1 7 1 8 1 9 2 10 1 11 1 12 1 13 1 14 1 15 1 16 1
          17 1 END
     BOND T 2 3 T 4 5 S 4 8 T 6 7 D 8 9 T 10 11 T 12 13 T 14 15 T 16 17 END
   END
   STR         ! Wgt =  1.75%
     LONE 1 2 2 1 3 2 4 1 5 1 7 1 8 1 9 1 10 1 11 1 12 1 13 1 14 1 15 1 16 1
          17 1 END
     BOND D 2 3 S 2 6 T 4 5 T 6 7 T 8 9 T 10 11 T 12 13 T 14 15 T 16 17 END
   END
   STR         ! Wgt =  1.75%
     LONE 1 2 2 1 3 1 4 1 5 2 6 1 7 1 9 1 10 1 11 1 12 1 13 1 14 1 15 1 16 1
          17 1 END
     BOND T 2 3 D 4 5 S 4 8 T 6 7 T 8 9 T 10 11 T 12 13 T 14 15 T 16 17 END
   END
```

```
   STR        ! Wgt =  1.75%
     LONE 1 2 2 1 3 1 4 1 5 1 6 1 7 1 8 1 9 1 11 1 12 1 13 1 14 1 15 2 16 1
          17 1 END
     BOND T 2 3 T 4 5 T 6 7 T 8 9 T 10 11 S 10 14 T 12 13 D 14 15 T 16 17 END
   END
   STR        ! Wgt =  1.75%
     LONE 1 2 2 1 3 1 4 1 5 1 6 1 7 1 8 1 9 1 10 1 11 1 13 1 14 1 15 1 16 1
          17 2 END
     BOND T 2 3 T 4 5 T 6 7 T 8 9 T 10 11 T 12 13 S 12 16 T 14 15 D 16 17 END
   END
   STR        ! Wgt =  1.75%
     LONE 1 2 2 1 3 1 4 1 5 1 6 1 7 1 8 1 9 1 10 1 11 2 12 1 13 1 15 1 16 1
          17 1 END
     BOND T 2 3 T 4 5 T 6 7 T 8 9 D 10 11 S 10 14 T 12 13 T 14 15 T 16 17 END
   END
   STR        ! Wgt =  1.75%
     LONE 1 2 2 1 3 1 4 1 5 1 6 1 7 1 8 1 9 1 10 1 11 1 12 1 13 2 14 1 15 1
          17 1 END
     BOND T 2 3 T 4 5 T 6 7 T 8 9 T 10 11 D 12 13 S 12 16 T 14 15 T 16 17 END
   END
 $END

$NRTSTRB
   STR        ! Wgt = 78.23%
     LONE 2 1 3 1 4 1 5 1 6 1 7 1 8 1 9 1 10 1 11 1 12 1 13 1 14 1 15 1 16 1
          17 1 END
     BOND T 2 3 T 4 5 T 6 7 T 8 9 T 10 11 T 12 13 T 14 15 T 16 17 END
   END
   STR        ! Wgt =  2.72%
     LONE 3 1 4 1 5 1 6 1 7 1 8 1 9 1 10 1 11 1 12 1 13 1 14 1 15 1 16 1 17 1
          END
     BOND S 1 2 T 2 3 T 4 5 T 6 7 T 8 9 T 10 11 T 12 13 T 14 15 T 16 17 END
   END
   STR        ! Wgt =  2.72%
     LONE 2 1 3 1 5 1 6 1 7 1 8 1 9 1 10 1 11 1 12 1 13 1 14 1 15 1 16 1 17 1
          END
     BOND S 1 4 T 2 3 T 4 5 T 6 7 T 8 9 T 10 11 T 12 13 T 14 15 T 16 17 END
   END
   STR        ! Wgt =  2.72%
     LONE 2 1 3 1 4 1 5 1 7 1 8 1 9 1 10 1 11 1 12 1 13 1 14 1 15 1 16 1 17 1
          END
     BOND S 1 6 T 2 3 T 4 5 T 6 7 T 8 9 T 10 11 T 12 13 T 14 15 T 16 17 END
   END
   STR        ! Wgt =  2.72%
     LONE 2 1 3 1 4 1 5 1 6 1 7 1 9 1 10 1 11 1 12 1 13 1 14 1 15 1 16 1 17 1
          END
     BOND S 1 8 T 2 3 T 4 5 T 6 7 T 8 9 T 10 11 T 12 13 T 14 15 T 16 17 END
   END
   STR        ! Wgt =  2.72%
     LONE 2 1 3 1 4 1 5 1 6 1 7 1 8 1 9 1 11 1 12 1 13 1 14 1 15 1 16 1 17 1
          END
     BOND S 1 10 T 2 3 T 4 5 T 6 7 T 8 9 T 10 11 T 12 13 T 14 15 T 16 17 END
   END
   STR        ! Wgt =  2.72%
     LONE 2 1 3 1 4 1 5 1 6 1 7 1 8 1 9 1 10 1 11 1 13 1 14 1 15 1 16 1 17 1
          END
     BOND S 1 12 T 2 3 T 4 5 T 6 7 T 8 9 T 10 11 T 12 13 T 14 15 T 16 17 END
   END
   STR        ! Wgt =  2.72%
     LONE 2 1 3 1 4 1 5 1 6 1 7 1 8 1 9 1 10 1 11 1 12 1 13 1 15 1 16 1 17 1
          END
     BOND S 1 14 T 2 3 T 4 5 T 6 7 T 8 9 T 10 11 T 12 13 T 14 15 T 16 17 END
   END
   STR        ! Wgt =  2.72%
     LONE 2 1 3 1 4 1 5 1 6 1 7 1 8 1 9 1 10 1 11 1 12 1 13 1 14 1 15 1 17 1
          END
     BOND S 1 16 T 2 3 T 4 5 T 6 7 T 8 9 T 10 11 T 12 13 T 14 15 T 16 17 END
   END
 $END
```

NRT of $[Sc(CO)_8]^-$

```
$NRTSTR
   STR        ! Wgt =  6.38%
     LONE 1 1 2 1 3 2 4 1 5 1 6 1 7 1 8 1 9 1 10 1 11 1 12 1 13 1 14 1 15 1
          16 1 17 1 END
     BOND S 1 2 D 2 3 T 4 5 T 6 7 T 8 9 T 10 11 T 12 13 T 14 15 T 16 17 END
   END
   STR        ! Wgt =  6.38%
     LONE 1 1 2 1 3 1 4 1 5 1 6 1 7 1 8 1 9 2 10 1 11 1 12 1 13 1 14 1 15 1
          16 1 17 1 END
     BOND S 1 8 T 2 3 T 4 5 T 6 7 D 8 9 T 10 11 T 12 13 T 14 15 T 16 17 END
```

```
  END
  STR         ! Wgt =  6.38%
    LONE 1 1 2 1 3 1 4 1 5 1 6 1 7 1 8 1 9 1 10 1 11 2 12 1 13 1 14 1 15 1
         16 1 17 1 END
    BOND S 1 10 T 2 3 T 4 5 T 6 7 T 8 9 D 10 11 T 12 13 T 14 15 T 16 17 END
  END
  STR         ! Wgt =  6.38%
    LONE 1 1 2 1 3 1 4 1 5 1 6 1 7 1 8 1 9 1 10 1 11 1 12 1 13 1 14 1 15 2
         16 1 17 1 END
    BOND S 1 14 T 2 3 T 4 5 T 6 7 T 8 9 T 10 11 T 12 13 D 14 15 T 16 17 END
  END
  STR         ! Wgt =  6.38%
    LONE 1 1 2 1 3 1 4 1 5 1 6 1 7 1 8 1 9 1 10 1 11 1 12 1 13 1 14 1 15 1
         16 1 17 2 END
    BOND S 1 16 T 2 3 T 4 5 T 6 7 T 8 9 T 10 11 T 12 13 T 14 15 D 16 17 END
  END
  STR         ! Wgt =  6.38%
    LONE 1 1 2 1 3 1 4 1 5 1 6 1 7 1 8 1 9 1 10 1 11 1 12 1 13 2 14 1 15 1
         16 1 17 1 END
    BOND S 1 12 T 2 3 T 4 5 T 6 7 T 8 9 T 10 11 D 12 13 T 14 15 T 16 17 END
  END
  STR         ! Wgt =  6.38%
    LONE 1 1 2 1 3 1 4 1 5 2 6 1 7 1 8 1 9 1 10 1 11 1 12 1 13 1 14 1 15 1
         16 1 17 1 END
    BOND S 1 4 T 2 3 D 4 5 T 6 7 T 8 9 T 10 11 T 12 13 T 14 15 T 16 17 END
  END
  STR         ! Wgt =  6.38%
    LONE 1 1 2 1 3 1 4 1 5 1 6 1 7 2 8 1 9 1 10 1 11 1 12 1 13 1 14 1 15 1
         16 1 17 1 END
    BOND S 1 6 T 2 3 T 4 5 D 6 7 T 8 9 T 10 11 T 12 13 T 14 15 T 16 17 END
  END
  STR         ! Wgt =  6.12%
    LONE 1 2 3 1 4 1 5 1 6 1 7 1 8 1 9 1 10 1 11 1 12 1 13 1 14 1 15 1 16 1
         17 1 END
    BOND S 1 2 T 2 3 T 4 5 T 6 7 T 8 9 T 10 11 T 12 13 T 14 15 T 16 17 END
  END
  STR         ! Wgt =  6.12%
    LONE 1 2 2 1 3 1 5 1 6 1 7 1 8 1 9 1 10 1 11 1 12 1 13 1 14 1 15 1 16 1
         17 1 END
    BOND S 1 4 T 2 3 T 4 5 T 6 7 T 8 9 T 10 11 T 12 13 T 14 15 T 16 17 END
  END
  STR         ! Wgt =  6.12%
    LONE 1 2 2 1 3 1 4 1 5 1 7 1 8 1 9 1 10 1 11 1 12 1 13 1 14 1 15 1 16 1
         17 1 END
    BOND S 1 6 T 2 3 T 4 5 T 6 7 T 8 9 T 10 11 T 12 13 T 14 15 T 16 17 END
  END
  STR         ! Wgt =  6.12%
    LONE 1 2 2 1 3 1 4 1 5 1 6 1 7 1 9 1 10 1 11 1 12 1 13 1 14 1 15 1 16 1
         17 1 END
    BOND S 1 8 T 2 3 T 4 5 T 6 7 T 8 9 T 10 11 T 12 13 T 14 15 T 16 17 END
  END
  STR         ! Wgt =  6.12%
    LONE 1 2 2 1 3 1 4 1 5 1 6 1 7 1 8 1 9 1 11 1 12 1 13 1 14 1 15 1 16 1
         17 1 END
    BOND S 1 10 T 2 3 T 4 5 T 6 7 T 8 9 T 10 11 T 12 13 T 14 15 T 16 17 END
  END
  STR         ! Wgt =  6.12%
    LONE 1 2 2 1 3 1 4 1 5 1 6 1 7 1 8 1 9 1 10 1 11 1 13 1 14 1 15 1 16 1
         17 1 END
    BOND S 1 12 T 2 3 T 4 5 T 6 7 T 8 9 T 10 11 T 12 13 T 14 15 T 16 17 END
  END
  STR         ! Wgt =  6.12%
    LONE 1 2 2 1 3 1 4 1 5 1 6 1 7 1 8 1 9 1 10 1 11 1 12 1 13 1 15 1 16 1
         17 1 END
    BOND S 1 14 T 2 3 T 4 5 T 6 7 T 8 9 T 10 11 T 12 13 T 14 15 T 16 17 END
  END
  STR         ! Wgt =  6.12%
    LONE 1 2 2 1 3 1 4 1 5 1 6 1 7 1 8 1 9 1 10 1 11 1 12 1 13 1 14 1 15 1
         17 1 END
    BOND S 1 16 T 2 3 T 4 5 T 6 7 T 8 9 T 10 11 T 12 13 T 14 15 T 16 17 END
  END
$END
```

Note that a large number of resonance structures are needed to denote each electronic structure, which can greatly complicate the interpretation process, and makes the comparison between the two complexes difficult (In the PIO analysis shown in Figure 6, 7 and S2, direct comparisons could be easily made because of the good correspondence between the PIO pairs). Moreover, it could be seen that the top 8 alpha Lewis structures of $Ca(CO)_8$ determined by NRT are all consist of Ca-O bonds, something that might be considered unphysical but was determined to have largest alpha contribution to the $Ca(CO)_8$ complex.