PECULIARITIES OF Cr-Cr BONDING. INSIGHTS FROM THE ANALYSIS OF DOMAIN AVERAGED FERMI HOLES

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Cr-Cr bonding

- Discovery of metal-metal bonding - 1970`s
  - Challenge for theoretical chemistry

- metal-metal bonds can have the character of multiple bonds
- multiplicity of these bonds can exceed the usual limits known from organic chemistry
Cr-Cr bonding

• Nature of metal-metal bonding is much more complex than anticipated by simple Lewis model

  • Simple electron sharing

  • New types of bonding interactions not considered in the Lewis model
Cr-Cr bonding

- Definition of DAFH

\[ g_\Omega(r) = 2 \int_\Omega \rho(r, r') dr' - \rho(r) \int_\Omega \rho(r') dr' \]
Cr-Cr bonding

- Methods of analysis

- diagonalization of the matrix representing the hole in appropriate basis

- graphical display of resulting eigenvectors
Interpretation of DAFH for the shared electron pair bonds

Example - acetylene $\Omega = \text{CC}$

- $N_{1,2} = 2.00$ (1s$^2$)
- $N_{3,4} = 1.150 \sigma_{(\text{CH})}$
- $N_{5} = 2.00 \sigma_{(\text{CC})}$
- $N_{6,7} = 2.00 \pi_{(\text{CC})}$
Interpretation of DAFH for the shared electron pair bonds

Example - acetylene $\Omega = \text{CH}$

- $N_1 = 1.997 \ (1s^2)$
- $N_2 = 1.948 \ \sigma_{(\text{CH})}$
- $N_3 = 1.000 \ \sigma_{(\text{CC})}$
- $N_{4,5} = 1.000 \ \pi_{(\text{CC})}$
Cr-Cr bond

• 2 recently studied complexes (Kriesel et al., Noor et al.) possess

• Extremely short Cr-Cr bond length (1.75-1.80 Å)

• 5 electron pairs available for metal-metal bonding

• Cr-Cr bond should be a quintuple bond
Cr-Cr bond

• Despite availability of 5 bonding electron pairs, the calculated Cr-Cr bond order is close to 4

• Similar discrepancy between the number of available electron pairs and bond multiplicity observed also for other metal metal bonds
  • Ga-Ga bond
  • Re-Re bond
Cr-Cr bonding

- Multiplicity of Cr-Cr bond?
- Nature of the bonding interactions?

- DAFH analysis revealed the nature of the bonding interactions
Cr-Cr bonding

- Complex I
- Extremely short Cr-Cr distance 1.80 Å
- 5 available bonding electron pairs
- Calculated Cr-Cr bond order 3.94
Cr-Cr bonding

- Complex II
- Extremely short Cr-Cr distance 1.75 Å
- 5 available bonding electron pairs
- Calculated Cr-Cr bond order 4.35
Cr-Cr bonding

• Computational methods used
  • Complex I     BLYP/6-311G
  • Complex II    BLYP/TZVP
Cr-Cr bonding domain $\Omega$  

- DAFH analysis complex I
  - 5 nonzero eigenvalue associated with metal-metal bonding
  - 4 eigenvalues close to 2 – electron pairs of Cr-Cr bond
  - 1 eigenvalue close to 1.1?
Cr-Cr bonding

hole $\Omega$  Cr-Cr

DAFH analysis complex II

- 5 nonzero eigenvalue associated with metal-metal bonding
- 4 eigenvalues close to 2 – electron pairs of Cr-Cr bond
- 1 eigenvalue close to 1.6?
Cr-Cr bonding

- The delocalization of one of the bonding electron pairs results in the depletion of electron density in the Cr-Cr domain
- The elucidation of the origin of the observed depletion – DAFH analysis of complementary holes averaged over one Cr atom
Cr-Cr bonding domain $\Omega$  Cr

- DAFH analysis complex I
- Broken valences of Cr-Cr bonds
- 4 eigenvalues close to 1
- 1 eigenvalue close to 0.6
Cr-Cr bonding domain $\Omega$  Cr

- DAFH analysis complex II
- Broken valences of Cr-Cr bonds
- 4 eigenvalues close to 1
- 1 eigenvalue close to 0.8
Cr-Cr bonding

- Asymmetry of the picture suggests partial splitting of one of $\delta$ components of Cr-Cr bond

- Similar situation observed in F-F bonding
Cr-Cr bonding

• Similar asymmetry observed for the F-F bond even at equilibrium bond length
Cr-Cr bonding

• Cr-Cr bond is contributed to by 4 shared electron pairs
• Fifth weak component of the bond – antiferromagnetic coupling of Cr atoms
• Bond can best be classified as effective quadruple bond
Metal-metal bonding

- Spectrum of the bonding interactions in the realm of metal-metal bonding is much wider than expected by the classical Lewis model of shared electron pair
- Bonding interactions can be quite peculiar and often have no classical counterpart
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