Magneto-structural correlations in double-bridged \([\text{Cu}_2\text{F}_6]^2-\)

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Abstract. A direct approach for calculating magnetic coupling constants is presented. For the double-bridged copper dimer \([\text{Cu}_2\text{F}_6]^2-\) the results compare well with fully numerical calculations in local spin-density approximation.

1. Introduction
The magnetic interaction between spins localized at centres \(A\) and \(B\) may be described by the Heisenberg Hamiltonian. The (isotropic) Heisenberg coupling constant \(J\), estimating the strength and mode of the magnetic coupling, can be obtained from experimental data, empirical rules and numerical electronic structure calculations. However, by any of these three methods it is almost impossible to derive analytical formulas for magneto-structural correlations. For a dimer with one magnetic orbital per metal centre the coupling constant for superexchange may be written as:

\[
J = K_{AB} - 2 \left( H_{AB} + \Delta t \right) / U \quad [1,2].
\]

\(K_{AB}\) (potential exchange) is the exchange integral between the localized magnetic orbitals leading to ferromagnetic coupling. The second term, kinetic exchange, describes the antiferromagnetic contribution for nondegenerate magnetic orbitals and is roughly a function of the overlap integral between the magnetic orbitals. \(\Delta t\) is a bond charge integral [3] and negligibly small in this ionic compound. While both, \(K_{AB}\) and \(U\) are expected to vary only moderately with the bridging angle and bonding distance, \(H_{AB}\) strongly depends on geometry and thus represents the key parameter for understanding magneto-structural correlations.

2. Calculation of \(H_{AB}\)
In order to derive an analytical formula for \(J\), Anderson [1] suggested, in a first step, the solution of the two monomer problems which, in a second step, are combined to give the solution for the dimer. Formally this means building linear combinations of the magnetic orbitals of the monomers \(\psi^+\) and \(\psi^-\) to magnetic orbitals of the dimer \(\psi_+\), \(\psi_-\). Combining them again gives localized magnetic orbitals \(\psi_+\), \(\psi_-\) [2]. All integrals occurring in \(J\) have to be calculated with regard to these orbitals, and \(H_{AB}\) is obtained as half the energy difference between the magnetic orbitals of the dimer

\[
H_{xx} = \langle \psi_+ | H | \psi_+ \rangle = \frac{1}{2} \langle \psi_+ + \psi_- | H | \psi_+ - \psi_- \rangle = \frac{1}{2} (E_+ - E_-) \quad (1)
\]
With $E_{x,y}^{\text{mono}} = \langle \psi_{x,y}^{\text{mono}} | H | \psi_{x,y}^{\text{mono}} \rangle$, $H_{AB}$ may also be expressed in terms of monomer orbitals

$$H_{x,y} = \frac{1}{2} \left( E_{x}^{\text{mono}} \left( N_{x}^{+} - N_{x}^{-} \right) + E_{y}^{\text{mono}} \left( N_{y}^{+} - N_{y}^{-} \right) + 2 \langle \psi_{x}^{\text{mono}} | H | \psi_{y}^{\text{mono}} \rangle \left( N_{x}^{+} + N_{x}^{-} \right) \right)$$ (2)

The key problem is constructing appropriate monomer orbitals. This has already been achieved [4] by transforming the full multi-centre MO-Hamiltonian of the monomer into an atomic-like single-centre problem via orthogonalization of the metal d-orbitals to the ligand group-orbitals and subsequent diagonalization of the reduced eigenvalue problem. Simple analytical formulas have been derived by neglecting ligand-ligand interactions as well as metal 4s- and 4p-orbitals, both having only small effects on the magnetic coupling mechanism in this ionic compound. The calculation of the energy and the contributions to the magnetic monomer orbital is done in the same way and uses the same notation.

Two different procedures for calculating $H_{AB}$ analytically will be discussed on the example of a double-bridged $\left[ \text{CuF}_{6} \right]^{2-}$ dimer with symmetry $D_{2h}$ that are denoted as the monomer and the dimer approach, respectively. In the monomer approach, following the original suggestion of Anderson, the energy of the magnetic orbital of the monomer with symmetry $C_{2v}$ is calculated first. Since a perturbational approach for the diagonalization of the Hamiltonian matrix has turned out to be too inaccurate for a system of lower symmetry, just the small contributions of ligand s-orbitals are accounted in a perturbational way in order to reduce the dimension of the matrix. The subsequent diagonalization of the reduced matrix is performed with two different methods. In the first one, the diagonal elements of the ligand p-orbitals are averaged. This approximation is well justified in ionic compounds when terminal and bridging ligands are the same and ligand-ligand interactions are weak so that the orbital energies of the different ligands are very similar. The energy of the magnetic monomer orbital at site $A$ directly corresponds to the highest eigenvalue of the matrix that can easily be diagonalized analytically in this reduced form. The respective eigenvector is obtained as

$$\left| \psi_{A}^{\text{mono}} \right\rangle = N_{A} \left( \alpha_{i}^{A} \cdot \left| \phi_{i}^{A} \right\rangle + \sum \gamma_{i}^{A} \cdot \left| \varphi_{i}^{A} \right\rangle \right)$$ (3)

where $\alpha_{i}^{A}$ and $\gamma_{i}^{A}$ are the coefficients for the ligand orthogonalized d-orbital $\left| \phi_{i}^{A} \right\rangle$ [4] and the symmetry adapted linear combinations for the ligand orbitals $\left| \varphi_{i}^{A} \right\rangle$, respectively.

In the second method, the contributions from the terminal ligands are assumed to cancel to a large extent in the difference $E_{+} - E_{-}$ (equation 1). Hence, only the bridging ligands are explicitly included in the eigenvalue problem, whereas the s-orbitals may be treated again in a perturbational way, leading to lower dimensional matrices. This alternative way is preferable when the energy difference between the p-orbitals of terminal and bridging ligands is large so that averaging is not reasonable. From the eigenvectors, equation (3), of the monomers the nondiagonal element $H_{AB}^{\text{mono}} = \langle \psi_{x}^{\text{mono}} | H | \psi_{y}^{\text{mono}} \rangle$ as well as the overlap integral $S_{x,y}^{\text{mono}} = \langle \psi_{x}^{\text{mono}} | \psi_{y}^{\text{mono}} \rangle$ can directly be calculated.

For symmetric dimers, where the two centres $A$ and $B$ are symmetry related, the decomposition into monomers may be less convenient. Therefore, in the dimer approach the energy difference $H_{AB}$ is calculated directly with respect to dimer orbitals. Therefore symmetric and unsymmetrical linear combinations of the group-orbitals are being built. The formalism still remains the same, the only difference being that two matrices, each corresponding to an irreducible representation of $D_{2h}$, have to be diagonalized where all group-orbitals are now linear combinations of atomic orbitals of both centres. The highest eigenvalues of the two matrices directly correspond to $E_{+}$ and $E_{-}$.
3. Calculation of $H_{AB}$ for a double-bridged $[\text{Cu}_2\text{F}_6]^{2-}$ complex for varying bridging angles

In order to investigate the suitability of the analytical approaches the results are compared with fully numerical calculations in local spin density approximation by the self-consistent charge Xα (SCC-Xα) method [5,6]. In these calculations, $H_{AB}$ corresponds to the half of the energy difference of the magnetic orbitals in the triplet state of the $[\text{Cu}_2\text{F}_6]^{2-}$ complex. As shown in figure 1, $H_{AB}$ is an approximately linear function of the bridging angle $\theta$, and changes its sign at about 92°.

All analytical calculations are based on the following approximation for matrix-elements between atomic orbitals [4]:

$$H_{ij}^{xy} = \frac{1}{2} \left( H_{ij}^{xx} + H_{ij}^{yy} + 2 \cdot U_{ij}^{xy} \right) \cdot S_{ij}^{xy} \quad (4)$$

where $\overline{U}_{ij}^{xy}$ is an averaged potential arising from the two and three centre integrals [4]. In order to analyze the effect of the simplifications of the Hamiltonian matrix in the analytical approaches, additionally, the Hamiltonian matrix with all ligands and without averaging the energies, is diagonalized numerically. The two methods for the analytical diagonalization yield the results in table 1. The eigenvectors have large contributions (>0.90) of Cu(3d), contributions of ligand p-orbitals between 0.2-0.3 and small but non-negligible ones from ligand s-orbitals (0.05-0.10). The energy difference $H_{AB}$ derived from the simplified matrices are very similar to the results of the numerical diagonalization, demonstrating that the analytical approaches indeed supply reasonable approximations for diagonalizing the eigenvalue problem.

Table 1. $H_{AB}$ as a function of the bridging angle calculated by different methods: the monomer (mon) and dimer (dim) approach, calculated with SCC-Xα method, numerical diagonalization (num), averaged ligand-energies (aver.) and bridging ligand only method (bridge). (in cm$^{-1}$)

| $\theta$ [°] | SCC-Xα | num. mon | aver. mon | bridge mon | num. dim | aver. dim | bridge dim |
|--------------|---------|-----------|------------|-----------|---------|----------|------------|
| 82.5         | -1339   | -1838     | -1865      | -1670     | -1934   | -2146    | -2347      |
| 90           | -363    | -977      | -1004      | -1085     | -1030   | -1041    | -1079      |
| 95           | 391     | -252      | -277       | -243      | -286    | -170     | -98        |
| 110          | 2823    | 1724      | 1720       | 2037      | 1714    | 2140     | 2493       |
| 125          | 4198    | 2966      | 2984       | 3467      | 2963    | 3648     | 4204       |

Figure 1. Visualization of the data of table 2. a) monomer approach; b) dimer approach

Both the analytical and numerical results for $H_{AB}$ within the dimer approach (table 1, figure 1b) agree in the same way as in the monomer approach. Hence, this analysis shows that at least for the symmetric double-bridged dimer, the monomer as well as the dimer approach represents an appropriate starting point for the calculation of $H_{AB}$. Finally, all analytical calculations exhibit a uniform shift of the zero-point up to about 96°, compared with the the SCC-Xα results, that may be
traced back to the neglect of ligand-ligand interactions, whereas the slopes of all curves are almost identical. Especially with respect to the simplifying model assumptions this must be considered as a fairly good result and confirms that the analytical approach is a suitable starting point for investigating magneto-structural correlations.

4. Correlation between $H_{AB}$ and the magnetic coupling constant $J$

As already mentioned in the introduction, the energy difference $H_{AB}$ should be the crucial parameter for magneto-structural correlations. Thus, the scaled negative of the square of $H_{AB}$ should reproduce the dependence of $J$ on the bridging angle $\theta$ obtained from the fully numerical electronic structure calculation with the broken symmetry formalism [7]. Using a scaling factor of $f = 1/6000$ and a constant term of $c = 30$, one obtains an almost perfect agreement between $J$ and $H_{AB}^2 \cdot f + c$, both taken from the fully numerical electronic structure calculations (figure 2), although this complex is a charge-transfer insulator, with $U \sim 10$eV and $\Delta_{CT} \sim 6$eV. Accordingly, $J$ has to be supplemented by a charge transfer term [8]. However, because $\Delta_{CT}$ is also almost constant, this term is implicitly contained in the parameter $f$. Therefore, the parameterized form of $J$ should be applicable to ionic Mott-Hubbard as well as to charge transfer insulators.

Since $J$ depends on the square of $H_{AB}$, even small deviations from the correct slope produce significant differences in the coupling constant as can be seen for the analytically derived $H_{AB}$ (figure 2). Nevertheless the analytical coupling constants still have the qualitatively correct dependence on the bridging angle and reproduce the range of ferromagnetic coupling quite well. Moreover, the comparison of $J$ with $H_{AB}^2$ distinctly demonstrates that the important term for magneto-structural correlations is indeed $H_{AB}$, at least in such an ionic compound.

![Figure 2. Comparison between $J$ and $H_{AB}^2 \cdot f + c$ with $f = 1/6000$ and $c = 30$; left: $H_{AB}$ from SCC-Xa; right: $H_{AB}$ from monomer (mon) and dimer (dim) approaches with different methods for diagonalization](image-url)

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