Metal–metal bonding in $Re_2Cl_8^{(2-)}$ from the analysis of domain averaged fermi holes

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Abstract The Re–Re bonding in anion $Re_2Cl_8^{(2-)}$, generally considered as a paradigm of quadruple metal–metal bond, was analyzed using the formalism of the analysis of domain averaged Fermi holes. The results of our analysis straightforwardly confirms the dramatic reduction of bond order of Re–Re bond reported in recent theoretical studies and provides simple chemically appealing description of the peculiarity of this bond bond. The analysis shows that although the Re–Re bond indeed involves four electron pairs, the bonding contribution of one of them, namely the one corresponding to δ bond is partially cancelled due to fractional population of antibonding δ^* orbital.

1 Introduction

The chemistry of compounds involving direct metal–metal bonds has undergone vigorous development in past 20–25 years [1]. The most important finding that stimulated the increasing interest in chemistry of metal–metal bonding was, that not only such bonds can exist but also that they can often have the character of multiple bonds [2]. An example in this respect is, e.g., the existence of triple MM bonds in molecules of the type M_2X_6 (M = W, Mo, X=NMe$_2$, OR etc) [3–5]. Moreover, the metal–metal bonds of higher than triple multiplicity have also been reported [6–15]. The most well known example of such systems is undoubtedly the ion $Re_2Cl_8^{(2-)}$, which represents the first synthetized representative of the molecule assumed to contain quadruple metal–metal bond.

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Because of its prominent position, the electron structure of this ion was the subject of numerous theoretical studies [16–20]. Conclusions of these studies repeatedly corroborated the original theoretical analysis on the basis of which the Re–Re bond in the ion $Re_2Cl_8^{(2-)}$ was generally accepted as a real paradigm for quadruple metal–metal bond. It was therefore of considerable interest when the structure of this ion was reconsidered in the two recent studies [21,22], using contemporary sophisticated post-Hartree–Fock (HF) computational tools. The most surprising and also the most challenging conclusion of these studies is, that contrary to general belief, the metal–metal bond in this ion can better be described as an effective triple bond. In view of these challenging findings it was of interest for us to see what picture of bonding will result for Re–Re bond from the analysis of domain averaged Fermi holes [23–29], that was recently applied to the analysis of the nature of metal–metal bond in several other transition metal complexes [26–28] and which, for example, confirmed the existence of quadruple W–W bond in $W_2Cl_8^{(4-)}$ [27]. As it will be shown, the results of our analyses confirm in very straightforward and visually appealing way the conclusions of the challenging studies [21,22], according to which the bonding contribution of one of four bonding electron pairs, namely the one corresponding to δ bond, is to considerable extent cancelled by the population of the anti-bonding metal–metal δ^* orbital so that the effective multiplicity of Re–Re bond drops to three.

2 Theoretical

As the formalism of the Fermi holes analysis is sufficiently described in the original literature [23–29], we consider it sufficient to summarize briefly only the basis ideas necessary for the purpose of this study.

The domain averaged Fermi holes are defined by Eq. (1)

$$g_\Omega(r_1) = N_\Omega \rho(r_1) - 2 \int_\Omega \rho(r_1, r_2) dr_2 \qquad (1)$$

where $\rho(r_1, r_2)$ and $\rho(r_1)$ are the pair density (diagonal element of second order density matrix) and the first order density respectively and Ω denotes the integration domain over which averaging is performed. The importance of these holes for structural investigations arises from the fact that the form of the Fermi hole (1) depends on how the domain Ω is actually chosen. This choice is in principle quite arbitrary but in previous studies we have shown that especially useful and chemically relevant information can be obtained if the domains Ω are identified with the atomic domains resulting from Bader's virial partitioning of the electron density function $\rho(r_1)$ [30]. In this case, namely, the hole provides the information about the actual valence state of a given atom in a molecule. In addition to domain associated with single atoms it is also possible to generate and analyze the holes associated with more complex domains formed by union of several atomic domains corresponding for example to various functional groups or interesting molecular fragments.

Although the formalism of domain averaged Fermi holes as defined by Eq. (1) is completely general and can be applied at any level of theory, the practical applications are still a bit restricted and require the adoption of several approximations. One of them concerns the pair density which, in the general case, should be derived from the correlated post-HF wave functions. Unfortunately extraction of this correlated pair density from existing quantum chemical programs is not a simple task and although the first example of the analysis of correlated DAFH was recently reported [31], most of the applications have so far been restricted to the holes generated at HF and/or also density functional (DFT) [32,33] level of the theory. In this connection it is, of course fair to say that the DFT extension, in which the pair density is formally constructed from Kohn–Sham orbitals using the Hartree–Fock-like formula, lacks strict theoretical justification and its success apparently relies only on the similarity of Hartree–Fock and Kohn–Sham wave functions. Nevertheless as the results of such a formal generalization proved to provide reasonable and realistic description of other metal–metal bonds [26–28], we believe that the above approach can be considered as feasible alternative especially for the applications in inorganic chemistry where DFT theory represents the contemporary computational standard.

The second approximation we had to adopt is related to the fact that the calculations on transition metal species often rely on the use of basis sets of ECP type. These basis sets, in which the electrons of inner shells are not treated explicitly but via effective core potential, are often know to produce the electron densities with corrupted topology which prevents the

determination of the Bader's atomic domains [33–36]. As a consequence, it is impossible to perform the integration over these domains and so the corresponding Fermi holes cannot be generated. In order to overcome this problem we have adopted an alternative simplified approach in which the integration over the real domain was replaced by the Mulliken-like approximation of the corresponding integrals, according to which the electron is in a domain of an atom A if it resides in the orbital centered at this atom.

The analysis of the Fermi holes, whether exact or generated via the above approximate approach, consists in the diagonalization of the matrix representing the hole in the appropriate basis of atomic orbitals and/or molecular orbitals and in the subsequent graphical inspection of the form of the eigenvectors associated with (essentially) nonzero eigenvalues of the corresponding hole. The details of such an analysis are sufficiently described in previous studies [23–29]. Here we therefore confine ourselves only to a brief summary reminding, e.g., that the analysis of the hole associated with a domain of a given single atom provides the information on the actual valence state of that atom in a molecule. Similarly, the Fermi holes associated with the more complex domain involving certain molecular fragments brings the information about the number and the nature electron pairs (bonds) whose splitting is formally required to isolate the given fragment from the original molecule as well as about the bonds and core and/or lone electron pairs which remain intact within the fragment. The nature of the electron pairs as well as the free valences is then straightforwardly revealed by the inspection of the corresponding eigenvectors.

3 Computations

Having summarized the basic ideas of the proposed approach let us report the results of our analysis of metal–metal bonding in the studied anion $Re_2Cl_8^{(2-)}$. This analysis requires two types of calculations. In the first step it is necessary to generate the wave function for completely optimized geometry of the corresponding molecule. In our case of the anion $Re_2Cl_8^{(2-)}$, these calculations were preformed at B3LYP/LANL2DZ and, for comparison, also BP86/LANL2DZ level of theory using Gaussian 98W program [37]. The resulting geometrical parameters are summarized in the Table 1. Consistent with the experimental observation, the optimized geometry of this ion corresponds to the eclipsed structure with D_{4h} symmetry and calculated geometrical parameters including, Re–Re bond length and Re–Re–Cl bond angles fairly well agree with the available experimental data [38, 39]. In addition to eclipsed conformation corresponding to the global minimum on the PE hypersurface we have also calculated the energy of the corresponding staggered structure so as to estimate the height of the rotational barrier

Table 1 Comparison of experimental and calculated geometrical parameters of $Re_2Cl_8^{(2-)}$ ion

Geometrical parameters	Calculated (bond lengths in pm, angles in degrees)[a]	Experimental (bond lengths in pm, angles in degrees)
R_{ReRe}	221	224[b]
	223	222[c]
R_{ReCl}	243	229[b]
	242	243[c]
ReReCl	105	104[b]
	104	104[c]

[a] Upper value corresponds to B3LYP, lower to BP86 functional
[b] Ref. [38]
[c] Ref. [39]

around ReRe bond. The calculated barrier (12.5 kcal/mol at B3LYP/LANL2DZlevel of the theory), surprisingly well agrees with the value 0.52 eV reported by Saito [22].

After having generated the wave function for the completely optimized ground state geometry of the ion, the second type of calculations consists in the generation and the analysis of the domain averaged Fermi holes for several selected molecular fragments. In our case the analysis was performed for the holes associated with the fragments $ReCl_4$ and ReRe. These calculations were performed using our own program WinFermi (available upon request) [40], which uses as an input the standard output file of Gaussian generated using the keywords POP=FULL and IOP(3/33=1) required to output the MO coefficients and overlap matrix whose knowledge is necessary for the analysis to be run. The results of these analyses are very little sensitive to the choice of the actual DFT functional and final values are summarized in Tables 2 and 3.

4 Results and discussion

In order to reveal the nature and the multiplicity of ReRe bond in $Re_2Cl_8^{(2-)}$, let us scrutinize first the Fermi hole associated with the fragment $ReCl_4$, formed by the symmetrical splitting of the molecule. In the light of what has been said above one can expect that the analysis of this hole should

provide the information about the bonds and core and/or lone electron pairs present in the fragment and, also, about the number of electron pairs (bonds) whose formal splitting is required to separate the fragment from the rest of the molecule. Let us now confront this expectation with the actual results. As it is possible to see from the Table 2, the analysis of this hole yields for both B3LYP and BP86 level of the theory 24 nonzero eigenvalues. Twenty of them are very close to two and as it will be shown they indeed correspond to electron pairs which are not affected by the formal splitting of the molecule. In order to get insight into the nature of these electron pairs it is useful to inspect the form of the corresponding eigenvectors. Such an inspection is shown in Fig. 1 which displays the eigenvectors obtained for the holes generated at B3LYP/LANL2DZ level of the theory. Such an inspections shows that first four of the eigenvectors correspond to ns and np core electron pairs on Re (Fig. 1a). In addition to these inner shell pairs, another four eigenvalues close to two are associated with eigenvectors corresponding to 4 electron pairs of ReCl σ bonds (Fig. 1b) present in the fragment, and the remaining 12 eigenvalues close to 2 correspond to lone electron pairs of 4 chlorine ligands (Fig. 1c). As expected, these electron pairs are not directly involved in ReRe bonding and need not be considered any further. The metal–metal bonding thus necessarily must be due to only the electrons associated with the remaining four nonzero eigenvalues with the actual values close to unity. The nature of

Table 2 Eigenvalues of the Fermi hole associated with the $ReCl_4$ fragment

Eigenvalue	Degeneracy	Interpretation
≈ 2	4	Electron pairs of ns and np inner shells on Re
≈ 2	4	Electron pairs of Re-Cl σ bond
≈ 2	12	Lone pairs on chlorine ligands
1.124[a]	1	"Broken valence" of ReRe δ bond
1.140[b]		
1.051[a]	2	"Broken valence" of ReRe π bonds
1.055[b]		
1.035[a]	1	"Broken valence" of ReRe σ bond
1.042[b]		

[a] B3LYP functional
[b] BP86 functional

Table 3 Eigenvalues of the Fermi hole associated with the fragment ReRe

Eigenvalue	Degeneracy	Interpretation
≈ 2	8	ns and np inner shell electron pairs on two Re atoms
≈ 2	1	Electron pair of Re–Re σ bond
≈ 2	2	Electron pairs of Re–Re (d–d) π bond
≈ 2	1	Electron pair of Re–Re δ bond
0.644[a]	8	"Broken valence" of Re-Cl σ bonds
0.652[b]		
0.595[a]	1	Partially populated δ^* orbital of Re–Re bond
0.642[b]		

[a] B3LYP functional
[b] BP86 functional
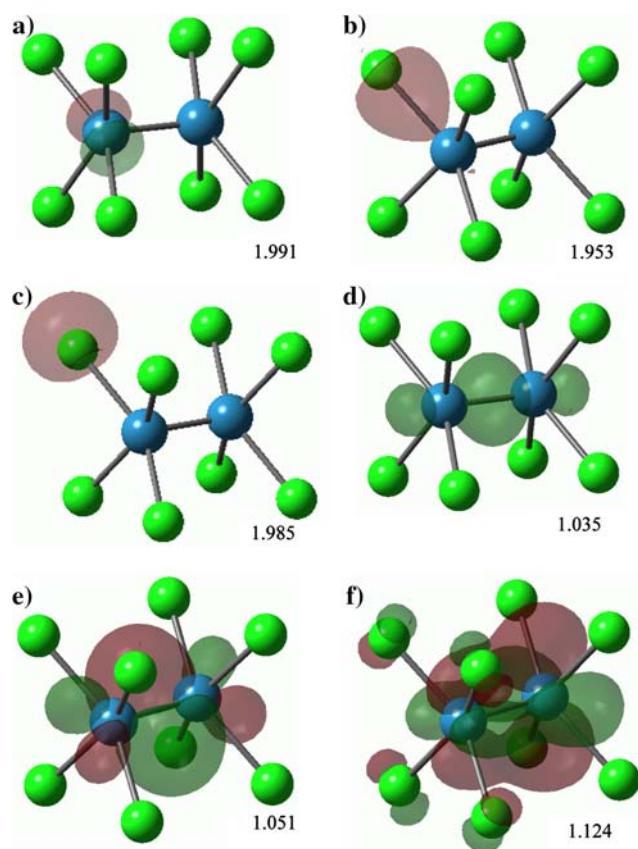
Fig. 1 Eigenvalues and eigenvectors of the Fermi hole associated with ReCl$_4$ fragment of the Re$_2$Cl$_8^{(2-)}$ ion. The pictures were generated at B3LYP/LANL2DZ level of the theory

Re–Re bond can straightforwardly be revealed by the inspection of the form of the corresponding eigenvectors. Thus for example, the eigenvalue equal to 1.035 is associated with the eigenvector which is very reminiscent of localized orbital of ReRe σ bond (Fig. 1d) and we interpret it as the "broken valence" of ReRe σ bond. In addition to this eigenvalue there is a pair of degenerated eigenvalues equal to 1.051 and the inspection of the corresponding eigenvectors shows (Fig. 1e) that they correspond to two components of broken

metal–metal (d–d) π bond. What remains is the eigenvalue equal to 1.124 and the inspection of the corresponding eigenvector (Fig. 1f) clearly shows that it corresponds to broken valence of metal–metal δ bond. We can thus see that the isolation of the ReCl$_4$ fragment from the rest of the molecule requires the formal splitting of four electron pairs which, consistent with original interpretation, seems indeed to suggest the Re–Re bond to be a quadruple bond. The situation is, however, a bit more complex. The clear indication of the peculiarity of Re–Re bond comes from the discrepancy between the number of electron pairs involved and the calculated bond order. Our value 2.8 calculated according to definition by Mayer [41,42] as well as the value 3.2 reported in the study [21] considerably deviate from what one would expect for "genuine" quadruple bond and because no similar reduction of bond order is observed in closely related case of W$_2$Cl$_8^{(4-)}$ ion it is evident that the nature of Re–Re bonding interactions is apparently more complex than originally assumed.

In order to reveal the origin of the peculiarity of Re–Re bond it is useful to complement the above analysis by the analogous analysis of the Fermi hole associated with the Re–Re fragment. The results of this analysis are summarized in the Table 3 from which one can see that the analysis of this hole yields for both B3LYP and BP86 functionals 21 nonzero eigenvalues, of which 12 are close to 2 and the remaining 9 are close to 0.6. The inspection of the form of the corresponding eigenvectors (Fig. 2) suggests that eight eigenvalues close to two correspond to eight electron pairs in ns and np inner shells of two Re atoms (Fig. 2a, b). These pairs are similar to those which were also detected in the analysis of the ReCl$_4$ fragment, only their number is doubled. In addition to these electron pairs which again are not relevant for bonding, there are another four eigenvalues close to two and as it is possible to see from the Table 3, the corresponding eigenvectors are clearly reminiscent of Re–Re σ bond, two components of Re–Re π bond and Re–Re δ bond (Fig. 2c–e). This result implies, similarly as in the previous case of the hole associated with ReCl$_4$ fragment, that the metal–metal bonding involves four electron pairs. Up to here
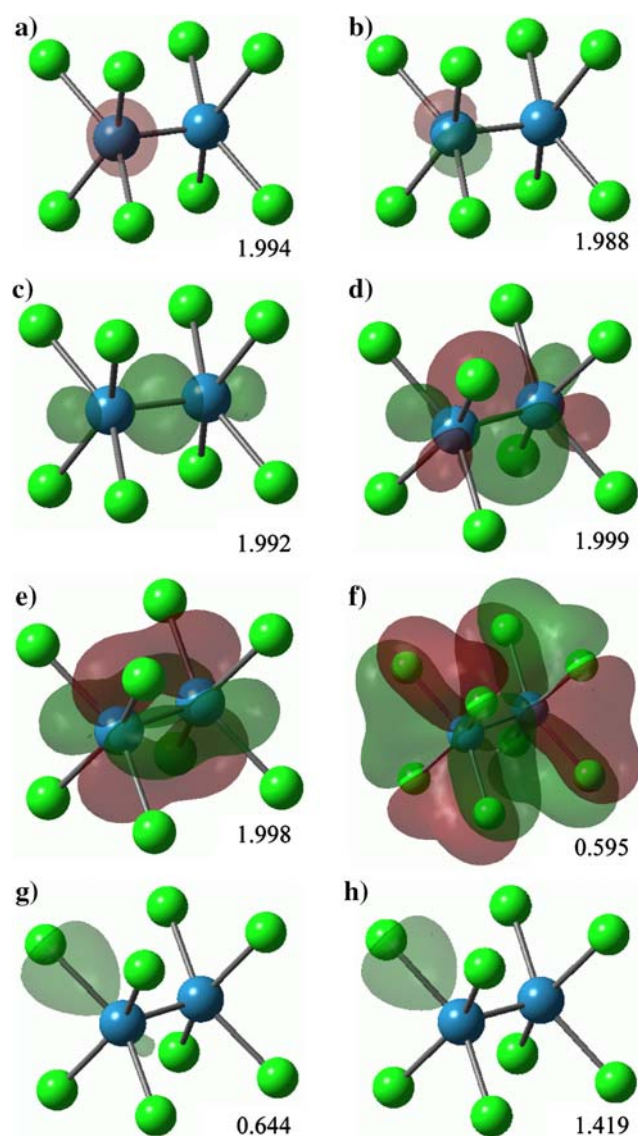
Fig. 2 Eigenvalues and eigenvectors of the Fermi hole associated with ReRe fragment of the $Re_2Cl_8^{(2-)}$ ion. The pictures were generated at B3LYP/LANL2DZ level of the theory

there is thus nothing unusual and the picture of bonding based on the above results is again consistent with the anticipated existence of quadruple Re–Re bond.

Such a straightforward interpretation is nevertheless slightly premature, because there still remain other nonzero eigenvectors of the Re–Re Fermi hole which were not so far taken into account and as it will be shown it is just here where is the clue to the elucidation of the origin of the observed decrease of calculated bond order.

The crucial role in completing the final picture of bonding in $Re_2Cl_8^{(2-)}$ belongs to nonzero eigenvalue equal to 0.595. The inspection of the form of the corresponding eigenvector shows, namely, that it is very reminiscent of antibonding δ^* orbital of Re–Re bond (Fig. 2f) .This result is very interesting

since the population of antibonding Re–Re δ^* orbital, which partially cancels the bonding contribution of δ orbital, was identified as the main mechanism of reducing the multiplicity of Re–Re bond also in the studies [21,22].

The above picture of bonding of the Re–Re bond remains valid also after taking into account the remaining set of eight degenerated nonzero eigenvalues equal to 0.644. The inspection of the corresponding eigenvectors shows, namely, that each of the can be associated with the broken valence of ReCl σ bond (Fig. 2g). which evidently have nothing to do with metal–metal bonding. The fact that the eigenvalues deviate in this case from the unity can simply be attributed to the polarity of Re–Cl bond which results in the uneven sharing of electron pairs. The observed value 0.644 can thus be regarded as a contribution of Re to shared electron pair of Re–Cl bond. Remaining roughly 1.4 electrons thus have to come from the contribution of chlorine and this interpretation is straightforwardly supported by the analysis of the Fermi hole associated with one of the chlorine ligands. Such analysis yields four nonzero eigenvalues of which three are distributed in the range 1.88–1.83, and the remaining is equal to 1.42. In keeping with the expectations, the inspection of the corresponding eigenvectors shows that the first three of them correspond to one σ and two π lone pairs of the ligand, while the last eigenvector (Fig. 2h) is reminiscent of the broken valence of Re–Cl bond observed for the ReRe hole. This resemblance, together with the near complementarity of the corresponding eigenvalues (1.419 + 0.644 $\approx$ 2) suggests that the Re–Cl bond has the character of more or less normal albeit polar 2c–2e σ bond.

Besides elucidating the nature of Re–Cl bond, the analysis of the Fermi hole associated with the Cl ligand also provides a clear explanation for the observed partial population of the δ^* bond. The inspection of Fig. 2f suggests, namely, that the eigenvector corresponding to this bond is evidently delocalized over the lone pairs of Cl ligands and the partial population of δ^* bond can thus be attributed just to the flow of electrons from the lone pairs of ligands. This flow is straightforwardly evident from the deviations of the corresponding eigenvalues (1.83–1.88) compared to ideal value of 2 observed usually for other lone and/or core electron pairs. This result is very interesting since similar flow of electron density from the ligand lone pairs to antibonding δ^* orbital is much smaller in the case of $W_2Cl_8^{(4-)}$ ion so that no dramatic drop of bond order takes place and the W–W bond is thus much better representative example of quadruple metal–metal bond.

In this connection it is, nevertheless fair to say that despite considerable reduction of Re–Re bond order, the cancellation of the bonding contribution of δ bond by the partial population of δ^* bond is not complete so that there still remains a slight contribution of δ bond. The existence of this bond is usually being associated with the preference of the eclipsed conformation of $Re_2Cl_8^{(2-)}$ ion, but the more detailed

scrutiny of the picture of bonding in eclipsed and staggered conformations seems to suggest that such a traditional interpretation is apparently slightly oversimplified. The first indication questioning the above straightforward interpretation comes from the comparison of calculated Re–Re bond orders where the value for staggered conformation (2.82) is even slightly higher than for the eclipsed one (2.80). This seems to suggest that the rotation around Re–Re bond apparently has no dramatic effect on the nature of this bond and, consequently, the δ bond is not apparently associated with the conformational preference. Such a conclusion is straightforwardly corroborated by the results of the Fermi hole analysis. Thus, for example, the analysis of the hole associated with ReCl4 fragment of the stagerred conformation of $Re_2Co_8^{(2-)}$ ion also yields four eigenvalues close to one which again corresponds to the splitting of four electron pairs involved in ReRe bond. Marginal effect of rotation around the Re–Re bond is also observed for the hole associated in the staggered conformation of the ion with the ReRe fragment. Similarly as in the case of eclipsed conformation one can again detect the existence of four bonding electron pairs, as well as the partial cancellation of the bonding contribution of δ bond. To demonstrate the close resemblance, the pictures of the eigenvectors corresponding to "skewed" σ, π and δ bonds, together with the partially populated δ^* bond are summarized in Fig. 3.

The partial cancellation of the bonding contribution of δ bond is interesting not only as a phenomenon complicating the analysis of the nature of Re–Re bond, but also because
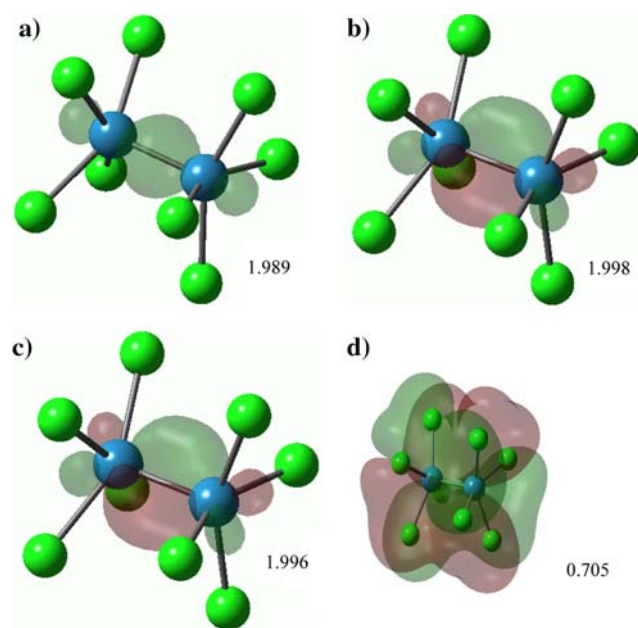
it shows the limitations of traditional bonding models and paradigms when one tries to apply them beyond the scope of classical bonding situations for which they were originally designed. This is often the case of transition metal chemistry and especially in the realm of metal–metal bonding the ambiguities in the classification of their nature are quite common [11,12]. In the case of Re–Re bond the situation can be best demonstrated by the quotation from the study [43]. "Whether it should be called a triple or quadruple bond or whether the δ bond should be called a weak bond or half bond is more or less a matter of the definition of the term bond or bond order" Similarly, albeit using slightly different words characterize the peculiarity of Re–Re bond the authors of the study [21]: "The alternatives are to describe the bonding as weak quadruple bond or as a bond involving four pairs with the effective bond order of about three. The latter model is more precise" and this is exactly the same what we found also in our analysis.

Summarizing the above results it is possible to conclude that the close parallel between the picture of the bonding based on the analysis of DAFH and the numerical results of sophisticated quantum chemical calculations used in the studies [21,22] is indeed encouraging and we believe that because of its relative simplicity, the above analysis could hopefully be used as a new efficient tool for the visualization of the structure of other molecules with complicated bonding pattern. This is, for example the case of metal–metal bonds in simple diatomic clusters where similar discrepancies between the maximal anticipated bond multiplicity and actually calculated bond order were recently reported [12]. To contribute to the existing debate concerning the nature of multiple metal–metal bonds we are currently considering the application of the formalism of domain averaged Fermi holes to the analysis of the bonding situation in series of diatomic metal clusters with the special focus on the comparison of the picture of bonding based on the Fermi holes derived from explicitly correlated CASSCF pair densities with the approximate DFT-like approach used in this study.

Fig. 3 Eigenvalues and eigenvectors of the Fermi hole associated with ReRe fragment of the staggered conformation of $Re_2Cl_8^{(2-)}$ ion. The picture was generated at B3LYP/LANL2DZ level of the theory

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