

Theoretical Investigations of the Chemical Bonding in $MM'O_2$ Clusters ($M, M' = \text{Be, Mg, Ca}$)

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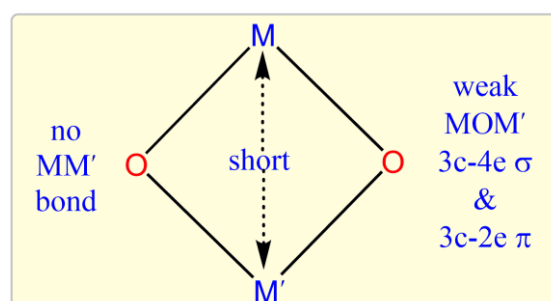
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Abstract

Motivated by the known stability of the somewhat unusual Be_2O_2 rhombus, which features a short BeBe distance but no direct metal-metal bonding, we investigate the nature of the bonding interactions in the analogous clusters $MM'O_2$ ($M, M' = \text{Be, Mg, Ca}$). CCSD/cc-pVTZ and CCSD(T)/cc-pVQZ calculations, amongst others, are used to determine optimized geometries and the dissociation energies for splitting the $MM'O_2$ clusters into metal oxide monomers. The primary tools used to investigate the chemical bonding are the analysis of domain-averaged Fermi holes, including the generation of localized natural orbitals, and the calculation of appropriate two- and three-center bond indices. Insights emerging from these various analyses concur with earlier studies on the M_2O_2 rhombic clusters in denying the existence of direct metal-metal bonding in the $MM'O_2$ rings, while detecting the presence of weak three-center (3c) bonding in the MOM' moieties. In general terms, these mixed $MM'O_2$ clusters exhibit features that are intermediate between those of M_2O_2 and M'_2O_2 , and the differences between the M and M' atoms appear to have relatively little impact on the overall degree of 3c MOM' bonding.



Keywords

$MM'O_2$ rings; Short metal-metal distances without direct bonding; Domain-averaged Fermi hole analysis; Localized natural orbitals; multicenter bond indices.

Introduction

Extremely short interatomic distances in molecular systems are generally considered to signify the existence of strong bonding interactions between the corresponding atoms. Key examples in this respect include the binuclear complexes of transition metals such as Re, Cr, Mo and W, in which such interactions result in direct metal-metal bonds whose multiplicity often even exceeds the traditional limits known from organic chemistry [1-10]. A counterexample is provided by the recently reported unusual bonding situation in a Be_2O_2 molecule stabilized by two noble gas atoms ($\text{Ng}-\text{Be}_2\text{O}_2-\text{Ng}'$) [11] for which the unusually short BeBe distance is not supported by direct Be-Be bonding, with the same being true for the bare Be_2O_2 rhombus. In order to explore this surprising discovery in more detail, we recently reported [12] a systematic study of the picture of the bonding in three bare rhombic clusters M_2O_2 ($\text{M} = \text{Be}, \text{Mg}, \text{Ca}$) using theoretical tools involving various charge and energy decomposition methods. The analyses confirmed the conclusions of the original study [11] in denying the existence of direct metal-metal bonding but they also detected the presence of weak three-center (3c) MOM bonding. Our main aim in the present study is to complement our previous work [12] with an examination of the bonding interactions in the closely related mixed clusters $\text{MM}'\text{O}_2$ ($\text{M}, \text{M}' = \text{Be}, \text{Mg}, \text{Ca}$). In particular, we were interested to ascertain to what extent the descriptions of $\text{MM}'\text{O}_2$ would exhibit features that are intermediate between those of M_2O_2 and $\text{M}'_2\text{O}_2$. We also wondered about the eventual impact on the overall degree of 3c bonding in the MOM' moieties of the differences between the M and M' atoms.

Computational Methods

The level of theory selected in our previous study [12] for geometry optimizations of M_2O_2 rhombic clusters was all electron coupled-cluster theory with single and double excitation (CCSD) using standard cc-pVTZ basis sets. This choice was made (after various tests of other methods and basis sets) because it can be expected to give reliable results for all of the clusters, and it could be shown to give good agreement with experimental results for the three metal oxide monomers. For much the same reasons, as well as compatibility with the previous work [12], full geometry optimizations of the M_2O_2 molecules in D_{2h} symmetry and of the $\text{MM}'\text{O}_2$ molecules in C_{2v} symmetry were performed using all electron CCSD, as implemented in the MOLPRO software package [13,14], using standard cc-pVTZ basis sets, sourced from the EMSL Basis Set Exchange [15]. The dissociation energies to metal oxide monomers were calculated at these geometries using single point all electron CCSD(T)/cc-pVQZ calculations, taking the basis sets from the same source. For comparison, we also performed some B3LYP calculations.

Analysis of the bonding interactions was performed for the CCSD/cc-pVTZ descriptions using various theoretical tools, including the analysis of domain-averaged Fermi holes (DAFHs) [16-23] for which the domains were taken to be combinations of those that arise in Bader’s well-known quantum theory of atoms in molecules (QTAIM) [24]. Except for the special case of the domain of the whole molecule, for which we obtain localized natural orbitals (LNOs), full DAFH analysis formally requires not only the one-electron density but also the pair density. When the latter is not readily available we may use instead a very reliable one-electron approximation [21] that is based on the natural orbital occupation numbers [25]. It was noted in our previous work on M₂O₂ clusters [12] that the pictures of DAFH functions generated at the CCSD/cc-pVTZ level using the one-electron approximation were little changed from those obtained for full-valence CASSCF wavefunctions, explicitly using the pair density. The CASSCF and CCSD LNOs were also found to be very similar to one another. These observations provide additional confidence in our use here of the one-electron approximation [21] for the DAFH analysis of the CCSD/cc-pVTZ descriptions of the M₂O₂ and MM’O₂ clusters. This DAFH analysis, which includes the isopycnic [26] localization of natural orbitals, was supplemented with an examination of selected two-center (2c) and three-center (3c) bond indices.

Mayer has introduced an improved definition of 2c Wiberg-Mayer bond orders for correlated systems by replacing the spin-density matrix in the general expression by a suitably defined matrix **R** [27]. Amongst various advantages, such a formulation retrieves for correlated systems the same exact normalization that applies at the closed-shell SCF level. QTAIM-generalization [28] of this so-called ‘improved’ definition of Wiberg-Mayer 2c bond orders in the case of correlated singlet systems [27] leads to the following simple expression [22]:

$$W(\Omega_A, \Omega_B) = \sum_I \sum_J (\omega_I \omega_J + R_I R_J) \langle \phi_I | \phi_J \rangle_{\Omega_A} \langle \phi_I | \phi_J \rangle_{\Omega_B} \quad (1)$$

in which ϕ_I is a natural orbital with occupancy ω_I , $\langle \phi_I | \phi_J \rangle_{\Omega_A}$ is a domain-condensed overlap integral (in which the integration is restricted to the domain Ω_A), and $R_I^2 = \omega_I(2 - \omega_I)$. Total values of $W(\Omega_A, \Omega_B)$ can easily be decomposed into separate contributions from the σ and π systems.

Much the same strategy can be applied to the analogous Wiberg-Mayer-like definition of 3c indices, again replacing the spin-density matrix by **R**. The resulting expressions [23] do not, however, recover for correlated systems the exact normalization that applies for closed-shell SCF.

An alternative approach [29], motivated by the manner in which \mathbf{R} is defined [27], involves the introduction of a suitably defined matrix \mathbf{Q} [29], whose benefit is that it leads to indices that again satisfy the same exact normalization as in the case of closed-shell SCF. The corresponding QTAIM-generalized [28] ‘improved’ Wiberg-Mayer-like 3c index for correlated singlet systems (which maintains exact normalization) then takes the form [29]:

$$W(\Omega_A, \Omega_B, \Omega_C) = \frac{3!}{4} \sum_I \sum_J \sum_K (\omega_I \omega_J \omega_K + Q_I Q_J Q_K) \langle \phi_I | \phi_J \rangle_{\Omega_A} \langle \phi_J | \phi_K \rangle_{\Omega_B} \langle \phi_K | \phi_I \rangle_{\Omega_C} \quad (2)$$

where $Q_I^3 = \omega_I(2 + \omega_I)(2 - \omega_I)$. Total values of $W(\Omega_A, \Omega_B, \Omega_C)$ can also easily be decomposed into separate contributions from the σ and π systems. In practice, the rival definitions using either \mathbf{R} [23] or \mathbf{Q} [29] turn out to lead to very similar values for 3c bonding indices, and the correction terms are in any case rather small for the 3c quantities. This is because most of the improvement that leads to exact normalization affects instead the ‘monoatomic’ $W(\Omega_A, \Omega_A, \Omega_A)$ terms.

All isopycnic localizations, DAFH analyses, and calculations of bond indices were performed using our own codes. The QTAIM analysis [24], including the calculation of domain-condensed overlap integrals, was carried out using AIMAll [30]. Pictorial depictions of LNOs and of DAFH functions were produced using Virtual Reality Markup Language (VRML) files generated with Molden [31], using the same isocontour value throughout.

Results and Discussion

Key bond lengths and angles for the optimized geometries of the clusters and of the metal oxide monomers are displayed in Figure 1. Analysis of the vibrational frequencies shows that all of these species represent true minima on the potential energy hypersurfaces. (The geometries for the M_2O_2 rings and for the metal oxide monomers are the same as reported previously [12].) Although they can easily be deduced from the information provided in Figure 1, it proves convenient to list in Table 1 the MM' distances, which are all fairly short, and the MOM' angles, which are typically less than 90° . (Not only is it clear from Table 1 that the MM' distance increases monotonically with the MOM' angle, but it turns out that there is a very strong quadratic correlation between these two quantities, as is shown in Figure S1 in the Supporting Information.) As was the case for the M_2O_2 systems [12], we find no evidence in the QTAIM analysis of the electron densities of any of these MM'O₂ rings for direct metal-metal bonding, in spite of the short MM' distances.

«Figure 1 near here»

«Table 1 near here»

Also listed in Table 1 are the dissociation energies for the $MM'O_2 \rightarrow MO + M'O$ splitting reactions, calculated using single point all electron CCSD(T)/cc-pVQZ calculations at the optimized CCSD/cc-pVTZ geometries. Clearly all six ring systems are stable with respect to this splitting to metal oxide monomers. Note that the dissociation energies for the M_2O_2 rings differ slightly from those reported previously [12] for which frozen core rather than all electron CCSD(T)/cc-pVQZ calculations were used; for completeness, we report in Table S1 in the Supporting Information the values based on the same level of theory as in the previous work. We also report in Table S2 in the Supporting Information the results from B3LYP calculations; we note that the various B3LYP/cc-pVTZ values are generally concordant with those from the CCSD and CCSD(T) calculations.

It is clear from the MM' distances, MOM' angles and dissociation energies (Table 1) that each mixed cluster is indeed intermediate between the corresponding M_2O_2 and M'_2O_2 systems, just as we might have expected. The same comment also applies to the calculated QTAIM-generalized 2c bond orders $W(M,M')$ (see Table 2), even though all of these values are rather small, in keeping with our expectations of there being no significant direct MM' bonding in any of these systems. It is clear from Table 2 that the relative contribution to $W(M,M')$ from the σ system dominates that from the π system in each case. (Traditional Wiberg-Mayer indices, which make use instead of simple summations over basis functions, turn out to have slightly higher values in the range 0.14 to 0.29, as is reported in Table S3 in the Supporting Information. These traditional Wiberg-Mayer indices also show more variation in the relative contributions from the σ and π systems, albeit with σ remaining the larger contributor in each case, but all of these quantities are still sufficiently small relative to typical values for 2c bonds for us to rule out the existence of any significant direct MM' bonding.)

«Table 2 near here»

Our results clearly confirm the conclusions of the previous studies [11,12] that also denied the existence of any significant degree of direct metal-metal bonding and so it was therefore of interest to investigate whether similar parallels hold also for the weak 3c bonding that was detected in the M_2O_2 systems [12]. For this purpose we performed a series of additional investigations, involving first the analysis of domain-averaged Fermi holes (DAFH) [16-23]. The usefulness of such holes for structural analysis arises from the fact that the information they provide depends on the type of domain over which the averaging is performed. It has been demonstrated in previous studies that the most interesting and chemically the most relevant information can be extracted from DAFH

analysis if the integration is over the QTAIM domains of individual atoms. In such a case, the holes provide information about the valence state of that atom in a molecule [32,33]. Analogous DAFH analysis can, however, also be performed for domains formed by the union of multiple QTAIM atomic domains, perhaps corresponding to certain functional groups or particularly interesting molecular fragments. In such cases, the holes provide information about the electron pairs (core, lone pairs or chemical bonds) retained in the fragment as well as about any broken valences created by the formal splitting of bonds that is required for isolation of that fragment from the rest of the molecule.

A special case for DAFH analysis is the domain formed by the union of all of the QTAIM atomic domains in the molecule, so that the integration is then over the whole space. It can easily be shown that DAFH analysis is then entirely equivalent to carrying out isopycnic localization [26] of the natural orbitals. Doing this for each of the clusters considered here, we found in each case a series of localized natural orbitals (LNOs, λ_i) that have occupation numbers (ν_i) close to two. In spite of such non-integer ν_i values, it is still convenient in the description that follows to refer to these LNOs as electron ‘pairs’. An examination of the LNOs thus allows the detection of all of the valence electron ‘pairs’ in the given molecule and can straightforwardly suggest their association with the distribution of chemical bonds, lone pairs, and so on. (Note that the small deviations of ν_i values from two are primarily due to electron correlation, given that the occupancies would be exactly two in the case of a single-determinant closed-shell description.)

The different sets of LNOs for the various $MM'O_2$ clusters turn out to be rather similar to one another and so we focus here on a representative example, namely $BeCaO_2$. In addition to a set of approximately doubly occupied functions that correspond to the various inner shells (and which contribute little, if anything, to the bonding), this analysis detects eight valence electron ‘pairs’. Two of these valence LNOs (see Figure 2), with occupancy 1.959 each, correspond to the electron ‘pairs’ of localized rather polar $Be-O$ σ bonds and a further two of them, with occupancy 1.954 each, correspond to the electron ‘pairs’ of localized rather polar $Ca-O$ σ bonds. Taken together, these four LNOs account for the main σ skeleton of the cluster. A further pair of LNOs, with occupancy 1.976 each, represent distorted $2s^2$ quasi-lone electron pairs on each oxygen atom. The remaining pair of LNOs, with occupancy 1.951 each, are based on $O(2p_\pi)$ functions but show distortions towards metal atoms that are suggestive of some degree of three-center two-electron ($3c-2e$) π bonding in each of the $BeOCa$ moieties. (Depictions of the analogous valence LNOs for all of the clusters are available in Figures S2-S7 in the Supporting Information.)

«Figure 2 near here»

Although the above results do not provide any indication of the existence of electron pairs that would correspond to a ‘genuine’ metal-metal bond, it was of interest to corroborate this conclusion by additional DAFH analysis for the domain involving both metal atoms (MM'). Given that such analysis provides information about the electron pairs (including chemical bonds) retained in the individual domains, the eventual presence of direct metal-metal bonding should be reflected by the existence of a corresponding DAFH function that is populated by roughly two electrons. As can clearly be seen from Figure 3, which again uses BeCaO₂ as our example, there are evidently no electron ‘pairs’ involved in direct metal-metal bonding.

«Figure 3 near here»

Also shown in Figure 3 are the dominant valence DAFH functions for one of the O domains in BeCaO₂, including pairs of symmetry-equivalent localized broken valences that are reminiscent of Be–O σ bonds (populated by 1.824 electrons each) and of Ca–O bonds (populated by 1.778 electrons each). Analysis of the hole associated with the BeCa fragment also provides two pairs of DAFH functions that are reminiscent of these metal-oxygen bonds, but instead populated by just 0.123 and 0.175 electrons, respectively, with the relative contributions from M and O reflecting the high polarity of these σ bonds. The near complementarity of the corresponding populations ($1.824 + 0.123 \sim 2$ and $1.778 + 0.175 \sim 2$) suggests that the σ bonding in each BeOCa fragment is essentially due to two electron ‘pairs’. As for the previously suggested $3c-2e$ π system, we observe a broken valence associated with the O fragment (populated by 1.844 electrons) while the BeCa domain contributes a further 0.092 electrons (albeit the shapes of the corresponding broken valences are in this case slightly more different). The remaining valence DAFH function shown in Figure 3, populated by 1.968 electrons, arises from analysis for the O domain and closely resembles the LNO for the distorted O($2s^2$) quasi-lone pair (see Figure 2).

Depictions of the analogous broken valences resulting from DAFH analysis for the MM' domain and for one of the O domains in each cluster are available in Figures S8-S13 in the Supporting Information. Although there are some variations in the low occupation valence DAFH functions arising from analysis of the MM' domain, with some of the resulting DAFH functions resembling in- and out-of-phase combinations of those we have described for BeCaO₂, the basic conclusions are essentially the same. In particular, there are evidently no electron ‘pairs’ involved in direct metal-metal bonding in any of the clusters.

The results of the above LNO and DAFH analyses are very interesting because alongside denying the existence of ‘genuine’ metal-metal bonds, they additionally also seem to provide evidence of a

degree of multicenter bonding that could explain the small $W(M,M')$ values in Table 2. As was demonstrated in an earlier study [34], the existence of 3c bonding in an ABC fragment requires the existence of non-vanishing bond orders between all pairs of atoms, AB, AC and BC. As such, the small $W(M,M')$ values could simply reflect residual interactions associated with weak 3c-2e and/or 3c-4e bonding. This, in turn, suggests that it could be useful to examine numerical values of so-called multicenter bond indices.

As is well known, multicenter bond indices were originally designed as a tool for detecting the existence of the then new bonding paradigm of sharing a bonding electron pair between more than two atoms [35-40]. The simplest example of such a situation is of course the idea of 3c bonding [41-43]. Various definitions of 3c bond indices have been shown to provide a straightforward numerical means for detecting the eventual existence of such bonding arrangements in molecules [44-46]. In the present work, we have used the QTAIM-generalized ‘improved’ 3c bond indices defined in Equation 2.

Before examining the calculations values of 3c bond indices for these clusters, it is useful to comment on their expected signs. In the case of the π system, the forms of the LNOs and DAFH functions for each MOM’ moiety clearly correspond to the topology depicted in Scheme I of Figure 4, in which each of the three atoms contributes via a single orbital. This topology does of course constitute a 3-center 3-orbital model [37], for which a simple analytical model predicts a positive sign for the 3c index in the case of 3c-2e bonding and a negative sign in the case of 3c-4e bonding. (The latter prediction has been confirmed by calculations on real systems [47].) On the other hand, the forms of the LNOs and DAFH functions for the MOM’ σ system are instead suggestive of a 3-center 4-orbital model [23], in which the central atom contributes via two orbitals, just as was observed for the central CBeC moiety in a formally zero-valent beryllium complex [23]. Adopting the bonding topology shown as Scheme II in Figure 4, which is clearly pertinent to the MOM’ σ system, a simple Hückel-like approach confirms the existence of non-vanishing positive 3c-4e indices [23], just as was observed in actual calculations [23].

« Figure 4 near here »

Although they are fairly small, the resulting values of the ‘improved’ 3c bond indices defined in Equation 2 are certainly not negligible for such a 3c index and, as can be seen from Table 3, they consist of positive contributions from both of the σ and π systems, with the former dominating in each case. The positive signs identify this weak 3c character as being 3c-4e in the σ system and 3c-2e in the π system. In order to corroborate further our interpretation of the nature and parentage

of the weak 3c bonding, especially that in the σ system, we present in Table S4 of the Supporting Information the results from a heuristic 3c generalization [23] of Cioslowski's covalent bond order [48], beyond the scope of traditional 2c-2e bonding. Those results concur with our classification of the weak 3c MOM' interactions as being predominantly 3c-4e σ bonding that is primarily associated with adjacent metal-oxygen bonds, augmented by a smaller component due to 3c-2e π bonding. We also observe from Table 3 that the differences between the M and M' atoms appear to have relatively little impact on the overall degree of 3c MOM' bonding in the MM'O₂ clusters.

«Table 3 near here»

Conclusions

We have investigated the structures and the nature of the bonding interactions in the clusters MM'O₂ (M, M' = Be, Mg, Ca). Calculations at the CCSD/cc-pVTZ level of theory were used to determine optimized geometries, all of which turned out to correspond to true energy minima. Subsequent single point CCSD(T)/cc-pVQZ calculations demonstrated that all of these clusters are stable with respect to dissociation into metal oxide monomers. The primary tools used to examine the chemical bonding in these clusters were DAFH analysis, including the generation of LNOs, and the calculation of appropriate 2c and 3c bond indices. Insights emerging from these investigations concur with earlier studies of M₂O₂ rings [12] in denying the existence of direct metal-metal bonding in the MM'O₂ clusters, while detecting the presence of weak 3c bonding in the MOM' moieties. The various analyses suggest the classification of the weak 3c MOM' interactions as predominantly 3c-4e σ bonding augmented by a smaller component due to 3c-2e π bonding. In general terms, the mixed MM'O₂ clusters were found to exhibit features that are intermediate between those of M₂O₂ and M'₂O₂, and the differences between the M and M' atoms appeared to have relatively little impact on the overall degree of 3c MOM' bonding.

Supporting information: Correlation of $r_{MM'}$ with $\theta_{MOM'}$; Dissociation energies from frozen core CCSD(T)/cc-pVQZ; Results using B3LYP calculations; Traditional two-center Wiberg-Mayer indices; Symmetry-unique valence LNOs for each of the clusters; Broken valences resulting from DAFH analysis for the MM' domain and for one of the O domains in each cluster; Results from a heuristic 3c generalization of Cioslowski's covalent bond order.

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Figure 1. Key geometric parameters for the various $MM'O_2$ clusters and for the metal oxide monomers.

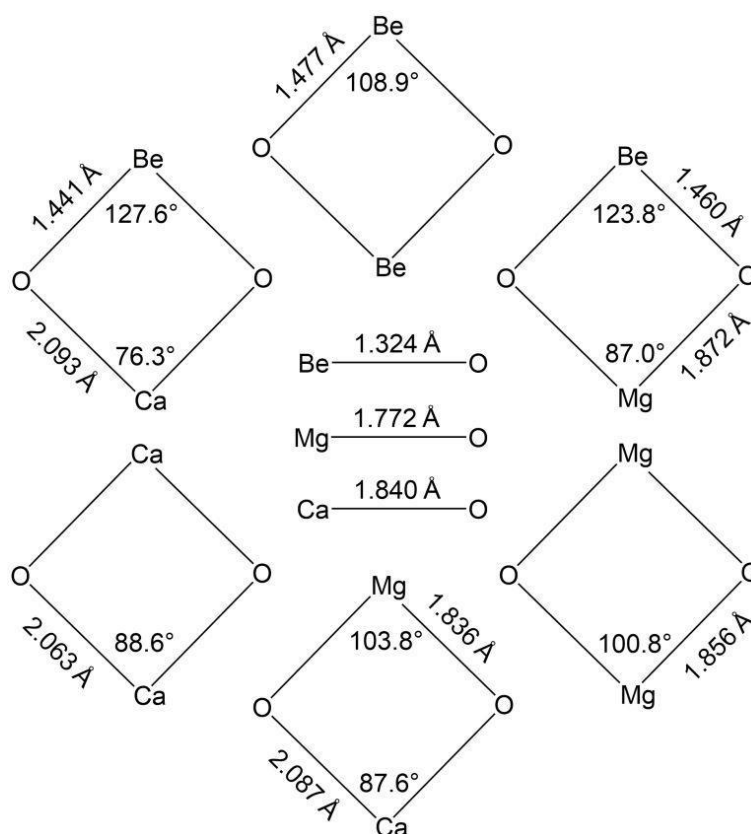


Figure 2. Symmetry-unique valence LNOs for $BeCa_2O_2$. (Molecular orientation as in Figure 1)

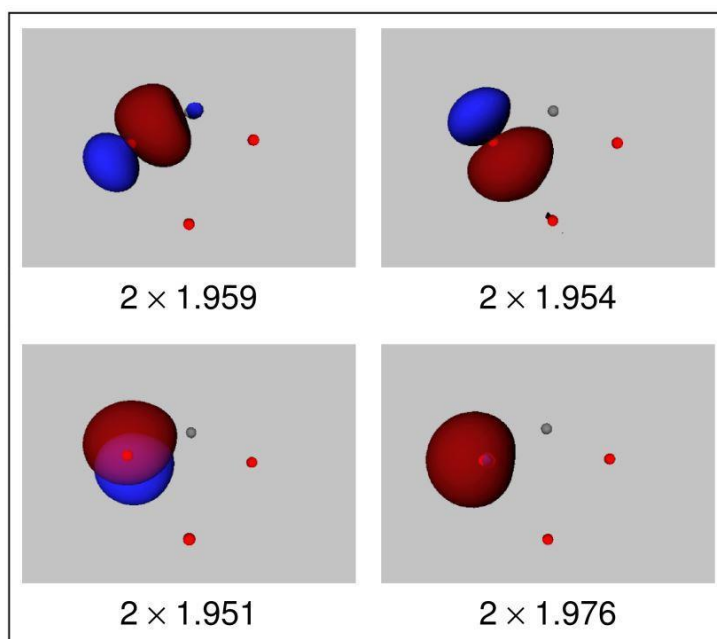


Figure 3. Broken valences resulting from DAFH analysis for the BeCa domain and for one of the O domains in BeCaO₂. (Molecular orientation as in Figures 1 and 2)

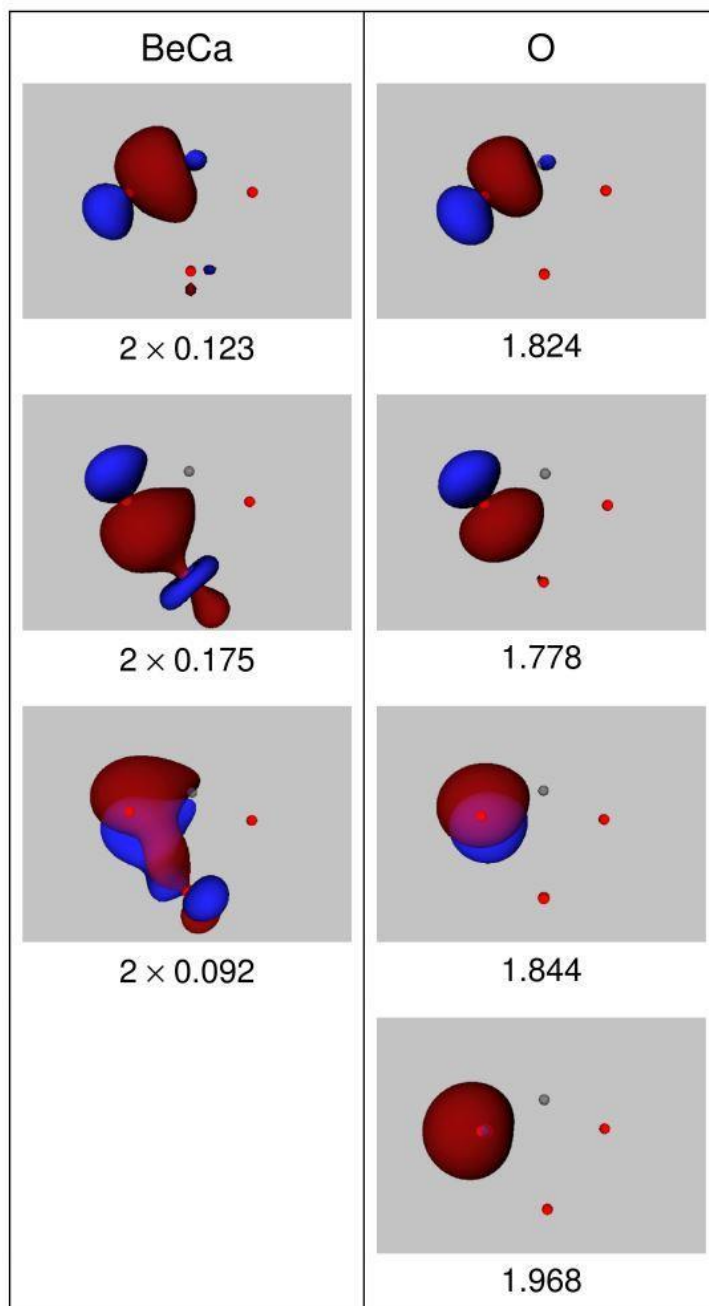


Figure 4. Three-center three-orbital and three-center four-orbital models of 3c-2e and 3c-4e bonding

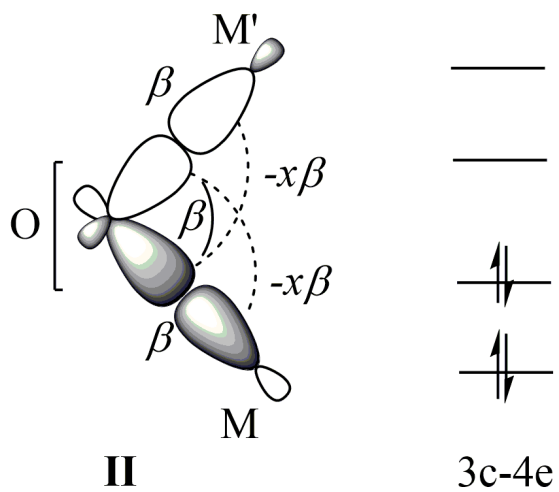
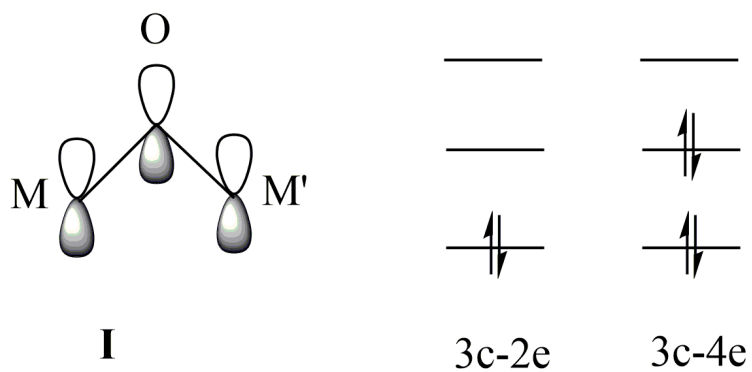


Table 1. Optimized MM' distances and MOM' angles (CCSD/cc-pVTZ level of theory) and dissociation energies for the splitting of MM'O₂ to metal oxide monomers, calculated at these geometries using CCSD(T)/cc-pVQZ.

M	M'	$r_{MM'}$ (Å)	$\theta_{MOM'}$ (°)	D_e (kcal/mol)
Be	Be	1.717	71.1	166
Be	Mg	2.046	74.6	157
Mg	Mg	2.367	79.2	135
Mg	Ca	2.639	84.3	133
Ca	Ca	2.954	91.4	126
Be	Ca	2.283	78.1	164

Table 2. QTAIM-generalized 'improved' 2c Wiberg-Mayer indices $W(M,M')$ (Equation 1) for MM'O₂ decomposed into relative contributions from the σ and π systems.

M	M'	$W(M,M')$		
		σ	π	total
Be	Be	76%	24%	0.020
Be	Mg	83%	17%	0.025
Mg	Mg	85%	15%	0.029
Mg	Ca	82%	18%	0.046
Ca	Ca	76%	24%	0.071
Be	Ca	78%	22%	0.034

Table 3. QTAIM-generalized 'improved' 3c Wiberg-Mayer indices $W(M,O,M')$ (Equation 2) for MM'O₂ decomposed into relative contributions from the σ and π systems.

M	M'	$W(M,O,M')$		
		σ	π	total
Be	Be	74%	26%	0.013
Be	Mg	82%	18%	0.015
Mg	Mg	83%	17%	0.018
Mg	Ca	81%	19%	0.027
Ca	Ca	74%	26%	0.041
Be	Ca	76%	24%	0.021