

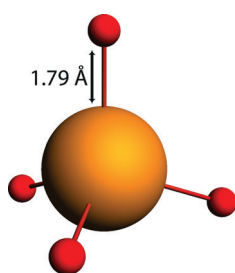
## Cesium's Off-the-Map Valence Orbital

Maarten G. Goesten,\* Martin Rahm, F. Matthias Bickelhaupt, and Emiel J. M. Hensen

**Abstract:** The  $T_d$ -symmetric  $[\text{CsO}_4]^+$  ion, featuring Cs in an oxidation state of 9, is computed to be a minimum. Cs uses outer core 5s and 5p orbitals to bind the oxygen atoms. The valence Cs 6s orbital lies too high to be involved in bonding, and contributes to Rydberg levels only. From a molecular orbital perspective, the bonding scheme is reminiscent of  $\text{XeO}_4$ : an octet of electrons to bind electronegative ligands, and no low-lying acceptor orbitals on the central atom. In this sense,  $\text{Cs}^+$  resembles hypervalent Xe.

Even if we realize that for some heavier elements the border between valence and core orbitals fades,<sup>[1]</sup> it could still be argued that hard-line distinction is only partially wrong at most; come what may, reactivity would feature the formal valence orbitals in some sort of role. But is that unflinchingly true? It is the first question in this work, in which we theoretically explore  $[\text{CsO}_4]^+$ , a molecule shown in Figure 1.

Electrons in core orbitals are often thought of as frozen. Whereas this helps reducing the cost of quantum-chemical calculations, there are cases in which these electrons play a significant role in electronic structure and bonding. There exists a pro-



**Figure 1.** The computed geometry of  $T_d$   $[\text{CsO}_4]^+$  at ZORA-PBE0/TZ2P, with its Cs–O bond length given in Å, orange Cs, red O.

fusion of recent literature on high-pressure effects in elemental solids. Sodium, lithium, and aluminum, under high pressures, all have their core orbitals overlap.<sup>[2]</sup> And this happens even for osmium, the most incompressible element.<sup>[3]</sup> In particular settings, such core overlap may push valence electrons to lattice interstitials, stripping the metal of conductivity, and forming what is referred to as an electride.<sup>[4]</sup> Direct effects on bonding occur, too: pressure was shown to turn cesium into a p block element, and mercury into a  $d^8$  transition metal.<sup>[5]</sup>

Cesium fascinates further. In a molecule, it does not require extreme conditions to use core orbitals for bonding. Hoffmann and co-workers showed that its occupied 5p orbitals contribute to holding  $\text{CsF}_5$  together.<sup>[6]</sup> Inspired by that work, and reports on  $[\text{IrO}_4]^+$  and  $[\text{PtO}_4]^{2+}$ ,<sup>[7]</sup> we wondered if  $[\text{CsO}_4]^+$  could feature Cs formally in an oxidation state of 9. We will see that the answer is yes, and that there is more to provoke the mind.

A 1982 publication by Spitsyn et al. (in Russian), discusses the possible existence of  $T_d$   $[\text{CsO}_4]^+$ . Its stability is ranked lower than that of  $\text{XeO}_4$ , but higher than that of  $\text{KrO}_4$ ,  $\text{ArO}_4$ , and  $[\text{RbO}_4]^+$ —enough for the possibility of the molecule's observation in experiment to be mentioned.<sup>[8]</sup> The neutral or anionic analogues,  $\text{CsO}_4$  and  $[\text{CsO}_4]^-$ , have received attention too. But the literature on these systems reports two distinct oxygen molecules that coordinate to the alkali metal, rather than a molecule of  $T_d$  symmetry.<sup>[9]</sup>

We start by assessing the thermodynamic and kinetic stability of  $T_d$   $[\text{CsO}_4]^+$ . Computation was carried out at ZORA-PBE0/TZ2P, with the ADF program.<sup>[10]</sup> The PBE0 functional, with inclusion of relativistic effects by ZORA, has been shown to give accurate results for cesium complexes.<sup>[11]</sup> Calculations predict that  $T_d$   $[\text{CsO}_4]^+$  is a local-minimum equilibrium structure, with all Hessian eigenvalues positive. Square-planar  $D_{4h}$   $[\text{CsO}_4]^+$  exists as a transition state between, and 53.7 kcal mol<sup>-1</sup> above, two tetrahedral minima with mutually inverted structures.  $T_d$   $[\text{CsO}_4]^+$  prefers a singlet state—the nearest triplet lies more than 43 kcal mol<sup>-1</sup> higher in energy. It features a large HOMO–LUMO gap, 4.68 eV, as computed at our level of theory.

Our minimum of interest is thermodynamically, highly unstable towards dissociation, as shown in Figure 2. Decomposition towards  $\text{Cs}^+$  and two molecules of oxygen proceeds in two steps, and via  $[\text{CsO}_2]^+$ . We investigated a direct, concerted decomposition towards two  $\text{O}_2$  molecules, but it appears to be a forbidden itinerary (Supporting Information, Section 12). The first step in the decomposition, from  $[\text{CsO}_4]^+$  to  $[\text{CsO}_2]^+$  and  $\text{O}_2$ , is aided by a change in spin state, which relates to the formation of triplet  $\text{O}_2$ . This also complicates determination of the associated barrier. We provide an estimate for the barrier, via a minimum energy pathway towards the geometry around which the transition occurs,

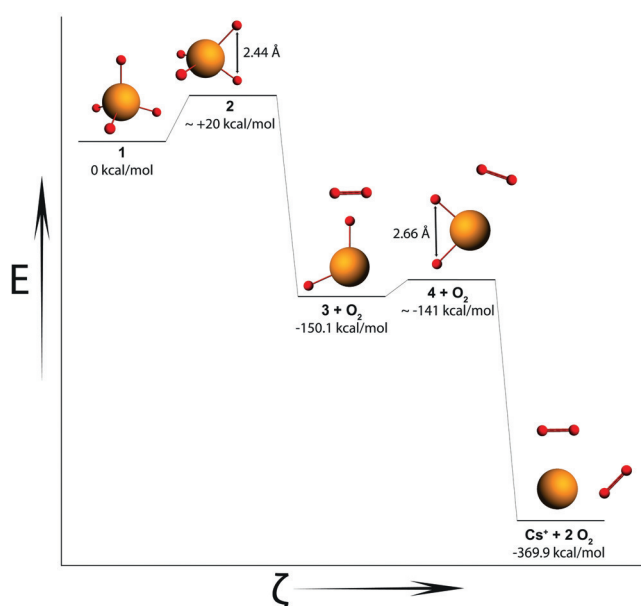
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**Figure 2.** Decomposition pathway of  $T_d$   $[\text{CsO}_4]^+$ . The energies are referenced against the parent structure, and the energy scale is schematic.

structure **2** in Figure 2. It lies about  $20 \text{ kcal mol}^{-1}$  above the parent structure. A similar spin transition occurs in the second step, from  $[\text{CsO}_2]^+$  to  $\text{Cs}^+$  and  $\text{O}_2$ , via structure **4**. Here, the barrier is lower, and below  $10 \text{ kcal mol}^{-1}$ . The Supporting Information, Section 11, contains the singlet and triplet potential energy surfaces associated with both steps.

On to the bonding in  $T_d$   $[\text{CsO}_4]^+$ , where we apply a fragment based approach; let us take geometry-optimized  $T_d$   $[\text{CsO}_4]^+$ , and slice it into  $\text{Cs}^+$ , one fragment, and  $[\text{O}]_4$ , the other fragment. We then analyze the fragment molecular orbitals (FMOs) of  $\text{Cs}^+$  and  $[\text{O}]_4$ , and explore the upshot of combining these in making up the electronic structure of  $[\text{CsO}_4]^+$ . For the  $\text{Cs}^+$  fragment, the computed FMOs are in essence the atomic orbitals we expect to interact. For the  $[\text{O}]_4$  fragment, the FMOs correspond to symmetry-adapted linear combinations of 2s and 2p atomic orbitals.

Our first look is to the gross Mulliken populations (MPs), computed for the FMOs, and listed in Table 1. The MPs indicate that cesium uses electrons of its outer core 5s orbitals in  $[\text{CsO}_4]^+$ : the population of 1.79 e is well down from 2.00 e, the value for non-interacting fragments. The charge transfer associated with the interaction, between the FMOs of  $A_1$  symmetry, occurs between cesium's core 5s orbital, and an initially unoccupied  $2A_1$  FMO of  $[\text{O}]_4$ .

Cesium's sub-valence 5p orbitals, of  $T_2$  symmetry, lose electrons upon interaction as well, and more so than the 5s. In this case, following charge transfer is more challenging, for we find some unanticipated d orbital populations.

Cesium's vacant  $4d_{xy}$ ,  $4d_{xz}$ , and  $4d_{yz}$  orbitals are of  $T_2$  symmetry, also. In principle, following a ligand-field line of thinking, these orbitals are prone to  $\sigma$ -overlap with suitable  $T_2$  FMOs of  $[\text{O}]_4$ . The same counts for the  $d_{x^2-y^2}$  and  $d_{z^2}$  orbitals, of  $E$  symmetry, and in that case  $\pi$ -overlap. We could conclude from Table 1 that all five d orbitals are significantly involved

**Table 1:** Gross Mulliken Populations (in e) of the fragment molecular orbitals of  $\text{Cs}^+$  and  $[\text{O}]_4$ . Cesium's FMOs are atomic orbitals—these are listed in an additional column.

Symmetry	$\text{Cs}^+$ Orbital	Population	$[\text{O}]_4$ Orbital	Population
$A_1$	5s	1.79	1 $a_1$	2.05
	6s	-0.02	2 $a_1$	0.22
$E$	$5d_{z^2}$	0.19	1 e	1.74
	$5d_{x^2-y^2}$	0.19	1 e	1.74
$T_1$	$4f_{x(z^2-y^2)}$	0.11	1 $t_1$	1.88
	$4f_{y(z^2-x^2)}$	0.11	1 $t_1$	1.88
	$4f_{z(x^2-y^2)}$	0.11	1 $t_1$	1.88
$T_2$	$5p_x$	1.15	1 $t_2$	1.98
	$5p_y$	1.15	1 $t_2$	1.98
	$5p_z$	1.15	1 $t_2$	1.98
	$5d_{xy}$	0.26	2 $t_2$	1.25
	$5d_{xz}$	0.26	2 $t_2$	1.25
	$5d_{yz}$	0.26	2 $t_2$	1.25
	$6p_x$	0.01	3 $t_2$	1.26
	$6p_y$	0.01	3 $t_2$	1.26
	$6p_z$	0.01	3 $t_2$	1.26

in the bonding picture as charge acceptors. More so, when looking at the orbital populations in  $T_1$  symmetry, we might argue that three of cesium's high-lying f orbitals play somewhat of a role in the bonding.

Truly, if cesium's s, p, d, and f orbitals were all involved, our bonding picture becomes knotty. But we will see that the essential bonding mechanism features little to no involvement of cesium's d and f functions, despite the computed orbital populations.

Before getting there, let us note an entire abstinence from interaction by cesium's 6s orbital—the MP is technically zero. This is formally the valence orbital that should govern reactivity, and in light of the first question posed in this Communication, an important observation. Inspection of the FMO coefficients of the  $A_1$  MO wavefunctions further supports this: the contribution of the  $\text{Cs}^+$  6s orbital is one to two orders of magnitude smaller than that of  $\text{Cs}^+$  5s, or the two  $[\text{O}]_4$  FMOs of that symmetry. It seems that cesium “skips” its valence orbital in bonding, using core (and possibly higher-lying) orbitals instead. What is the mechanism here?

A way to answer that question is to analyze the interaction between our two fragments in terms of energy per orbital symmetry.<sup>[12]</sup> This requires us to isolate the contribution of orbital interaction,  $\Delta E_{oi}$ , from the total interaction energy associated with bringing  $\text{Cs}^+$  and  $[\text{O}]_4$  together.  $\Delta E_{oi}$  describes stabilization by mixing, and charge transfer, between the FMOs of  $\text{Cs}^+$  and those of  $[\text{O}]_4$ —both occupied and virtual.<sup>[13]</sup> We calculate  $\Delta E_{oi}$  by an energy decomposition scheme, and refer to other publications for further details on the computational methodology.<sup>[14]</sup> We stress that energetically, this term makes up more than 80 % of the total stabilizing interaction—orbital interactions keep  $\text{CsO}_4^+$  intact (Supporting Information, Section 2).

Having established that, the key to unravelling the bonding mechanism is to break up  $\Delta E_{oi}$  in terms of irreducible representations of the  $T_d$  point group. Computed values are given in Table 2, left. The value for  $T_2$  symmetry is dominant, and more than an order of magnitude larger than all others. Is

**Table 2:** Left: energy decomposition of  $\Delta E_{oi}$  into terms of the irreducible representations of the  $T_d$  point group. Right: energy decomposition of  $\Delta E_{oi}$  into terms of the irreducible representations of the  $T_d$  point group with virtual  $T_2$  functions deleted for the  $\text{Cs}^+$  fragment.

Full TZ2P basis set		Virtual $T_2$ functions deleted	
Symmetry	$\Delta E_{oi}$ [kcal mol <sup>-1</sup> ]	Symmetry	$\Delta E_{oi}$ [kcal mol <sup>-1</sup> ]
$A_1$	-52.9	$A_1$	-51.5
$E$	-54.2	$E$	-55.8
$T_1$	-56.6	$T_1$	-57.8
$T_2$	-795.6	$T_2$	-736.0

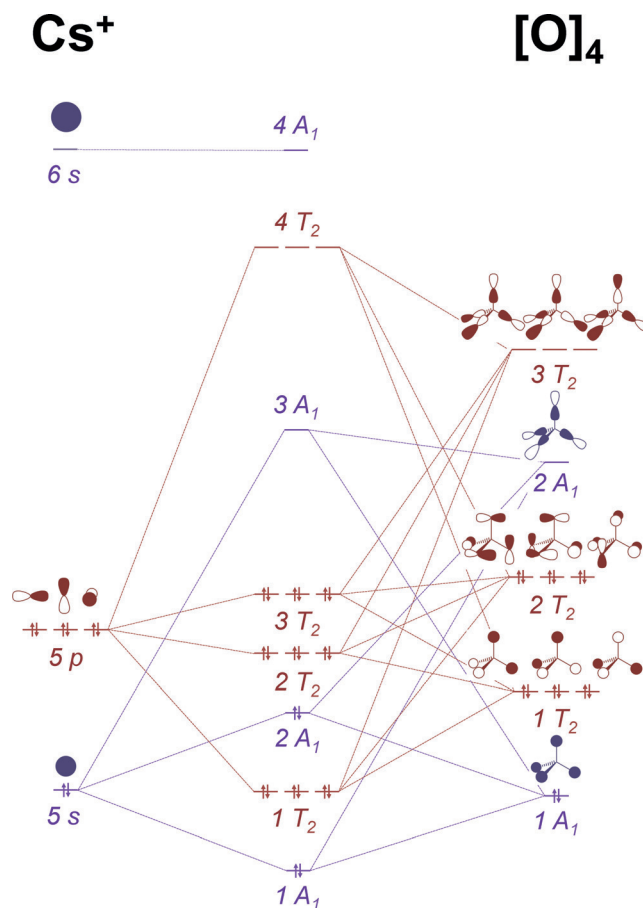
this stabilization connected to cesium's outer-shell d, or core p orbitals? We performed an additional decomposition analysis to investigate this. For this calculation, we have deleted the virtual functions of  $T_2$  symmetry for the  $\text{Cs}^+$  fragment from the TZ2P basis set, in order to extract a value for cesium's outer core 5p orbitals. The newly computed values are listed in the right part of Table 2. In comparison with the previously calculated energies, values for all symmetries but  $T_2$  have (gratifyingly so) barely changed. The decrease in stabilization for  $T_2$  amounts to a bit less than 60 kcal mol<sup>-1</sup>, which indicates that the  $d_{xy}$ ,  $d_{xz}$ , and  $d_{yz}$  functions do contribute relatively little to the bonding for that symmetry. Confusing as their populations may be, and typically encountered for hypervalent molecules, d (and f) orbitals act as polarization functions. As such, they improve the computed wavefunction, yet contribute little to the bonding energy.<sup>[15]</sup> Thus, we underline the value of an energy decomposition per symmetry in this work, to distinguish between functions and valence orbitals.

Stabilization for the  $A_1$  symmetry is low as well, even if we recognize that  $A_1$  is non-degenerate, and not doubly ( $E$ ) or triply ( $T_1$  and  $T_2$ ) so. This relates to the Cs 5s orbital, which lies very low in energy, with respect to the  $A_1$  FMOs of the  $[\text{O}]_4$  fragment.

To verify the insignificance (energy-wise) of the Cs 6s orbital in bonding, we deleted it from the TZ2P basis set, and performed another energy decomposition analysis. The ensuing, newly obtained orbital stabilization for  $A_1$  is no different from the original value within two numbers behind the decimal point (Supporting Information, Section 3).

The computed FMOs are in near-perfect harmony with those derived (by hand) with Group Theory. This is glee to the theoretical chemist; it allows for canonical representation in a diagram. With the results of Table 2 in hand, we can construct a diagram that summarizes the bonding well. This diagram is displayed in Figure 3. It lists the interacting FMOs by energy, but with an arbitrary scale that suits representation qualitatively.

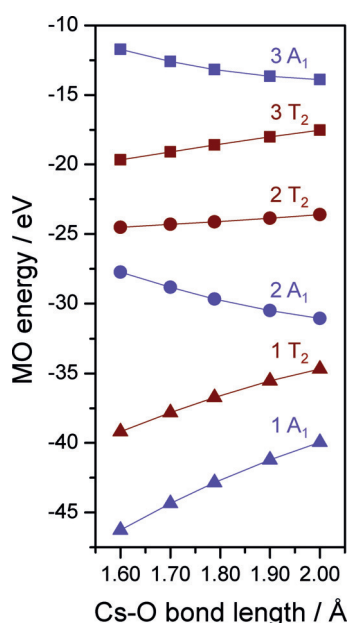
To gauge which of the  $[\text{CsO}_4]^+$  MOs are bonding, and which are antibonding, radial orbital-energy slopes (ROS) were calculated.<sup>[16]</sup> In this case, the Cs–O bond length is varied whilst keeping the  $T_d$  symmetry of the molecule intact. The response of the MO energies to the change in bond length is indicative of their character: an increase in energy with increasing bond length (that is, a positive slope) suggests bonding interaction. Similarly, a negative slope suggests antibonding, and (near)-flatness, nonbonding.



**Figure 3.** MO diagram of  $T_d$   $[\text{CsO}_4]^+$ , as interaction between a  $\text{Cs}^+$  ion and an  $[\text{O}]_4$  fragment. The interactions within  $A_1$  symmetry are in purple, those within  $T_2$  symmetry in red. To provide a clear 3D picture, the orientation of the  $[\text{O}]_4$  FMOs is angled with respect to that of the  $\text{Cs}^+$  p orbitals.

Analyzing the MO scheme in Figure 3, and the ROS curves in Figure 4, we start with the  $A_1$  symmetry. The bonding character of  $1A_1$  and antibonding character of 2 and  $3A_1$  are quickly revealed. As mentioned above, the orbital stabilization within  $A_1$  symmetry is minor, but our schematic bonding picture should still feature the  $A_1$  interactions; they involve  $3A_1$ , the LUMO level. And strikingly, this level features no involvement of cesium's 6s orbital either (Supporting Information, section 1).  $T_d$   $\text{CsO}_4$ , a reduced  $T_d$  analogue of our molecule, contains one electron in  $3A_1$ . This additional electron, with respect to  $[\text{CsO}_4]^+$ , enters the  $3A_1$  orbital, which is antibonding. Unsurprisingly, we obtain a larger value for the Cs–O bond length (1.842 Å), and  $\text{CsO}_4$  is not a minimum.

But where does cesium's valence 6s orbital come in, then? Up in energy by more than 8.5 eV from the LUMO, and ultimately off-the map, it makes up the  $4A_1$  level. When going from the LUMO to  $4A_1$ , we still find three  $4T_2$  levels in between, on the way. We conclude that cesium's valence orbital becomes important only when treating Rydberg states. In configurations near the ground state, it plays essentially no role.



**Figure 4.** Molecular orbital energy variations of  $T_d$   $[\text{CsO}_4]^+$  as a function of Cs–O separation distance.

For  $T_2$  symmetry, as drawn out in Figure 3, we have an electron-rich bonding pattern, similar to that for  $\text{XeO}_4$ , and we expect oxygen s–p mixing to play a role here. Moving again to the ROS curves in Figure 4, we see that  $1T_2$  is clearly bonding. And the slopes of the  $2T_2$  and  $3T_2$  levels are positive also, yet considerably flatter than that of  $1T_2$ . Taking the computed orbital overlap populations into account (Supporting Information, section 4), we regard  $2T_2$  as predominantly nonbonding, and  $3T_2$  as weakly bonding. In a nutshell, the ROS analysis confirms what we obtained from our decomposition scheme in Table 2 earlier: cesium's p orbitals hold  $[\text{CsO}_4]^+$  together.

With this work, we invite discussion on how we should look at cesium. For  $[\text{CsO}_4]^+$ ,  $\text{Cs}^+$  only uses its core orbitals for bonding. We do not think this is an exception. Following the work on star-shaped,  $D_{5h}$   $\text{CsF}_5$ ,<sup>[6]</sup> we computed  $C_s$   $\text{CsF}_7$  to be a minimum. Analyzing the bonding between a Cs and a  $[\text{F}]_7$  fragment, we derive that cesium uses its occupied 5p orbitals for bonding, omitting use of its valence 6s and other outer-shell orbitals (Supporting Information, Section 5).

If using only its outer core, we should envisage  $\text{Cs}^+$  to react as a Lewis base, and not as a Lewis acid. Indeed, we estimated interaction between  $\text{Cs}^+$  and common bases  $\text{NH}_3$  and  $\text{PH}_3$  to be quite weak (Supporting Information, section 6).

Note the difference with lithium, at the top of the same group, an element known for using outer-shell orbitals as electron acceptors.<sup>[17]</sup> For comparison,  $[\text{LiO}_4]^+$  was optimized within  $T_d$  symmetry. The molecule is not a minimum, but it is interesting to compare  $\text{Li}^+$  to  $\text{Cs}^+$ , in their interaction with  $[\text{O}]_4$ . The  $[\text{O}]_4$  cage is a Lewis acid, and with the inertness of the Li 1s orbitals, there is comparably little stabilization by orbital interactions on offer—a bit more than  $50 \text{ kcal mol}^{-1}$ , originating from donation into Li's valence p orbitals (Supporting Information, Section 7). Li and  $\text{Li}^+$  use outer-

shell orbitals to react with bases;<sup>[18]</sup> and we note the special case of neutral and bound  $\text{Li}(\text{NH}_4)$ , in which the unpaired electron resides in a mixture of Li 3s and  $\text{NH} \sigma^*$ -orbitals.<sup>[19]</sup> We will investigate the trend in basic and acidic properties along the first group of the Periodic Table (Li, Na, K, Rb, Cs) separately, in the future.

A calculation on a cesium atom, at the level of theory used in this work, reveals a gap of almost 12.9 eV between the singly-occupied HOMO, and the level next lower in energy (Supporting Information, Section 8). Even when we take this value only as indicative (and we should), it is hefty. A similar calculation on a xenon atom suggests a comparable (13.3 eV) HOMO–LUMO gap. We refer to a recent report by Miao et al. on magnesium-xenon mixtures at high pressures.<sup>[20]</sup> The authors predict charge transfer from the Mg 3s to the Xe 5d orbital, in the electronic structure make-up. The shell structure of such a Xe anion looks a bit like that of atomic Cs: 8 paired electrons in a relatively inert core, and an unpaired electron much higher in energy.

Let us say that the kinship is there—and refer to a circular version of the Periodic Table which connects cesium to xenon.<sup>[21]</sup> We may then wonder how the bonding similarities between  $\text{Cs}^+$  and electron-rich, hypervalent xenon establish themselves. The MO scheme in Figure 3 follows what we would draw out for  $T_d$   $\text{XeO}_4$  (and what we would compute; see Supporting Information, Section 9). Just as for hypervalent compounds, electronegative ligands, such as oxygen and fluorine will favor the stability of complexes  $\text{Cs}^+$  forms—these oxidize its core efficiently.

Regardless of any scheme or table, cesium appears an outlier—one that binds through the outer core, with a free electron to boot. It recently broke the record for highest coordination number, 16, in a confined tetracosahedral arrangement of F atoms.<sup>[22]</sup> And we sense it will feature in many new interesting molecules and materials.

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## Conflict of interest

The authors declare no conflict of interest.

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