Reaching the maximum multiplicity of the covalent chemical bond

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The maximum value is reached by the tungsten diatom, W$_2$. Periodic system, that the maximum bond multiplicity is six.

We show here, through a systematic study of the covalent chemical bond covering the entire chemical bond can have. As a result of the analysis, we show that the highest multiplicity that a combi to form this very strong bond. Before 1964, the triple bond; the three unpaired 2p electrons on each atom combine to form this very strong bond. 1964, the triple bond was assumed to be the highest multiplicity that a chemical bond can have. We show here, through a systematic study of the covalent chemical bond covering the entire periodic system, that the maximum bond multiplicity is six.

As many quantities used to describe what the electrons do in a molecule, the bond order is not a measurable quantity, for example, as a result of steric hindrance, then the value of $x$ may be quite different from zero. When the value is 0.5, for instance, the bond is only halfway formed and the effective bond order is $1-0.5=0.5$. In multiply bonded systems, the different orbitals forming the bonds may have different overlaps and $x$ may vary considerably from bond to bond.

This measure of the bond multiplicity is based on very well defined and stable quantities: the occupation numbers of the natural orbitals (NOs). It can only be used together with wave functions that give realistic values for these quantities. These are by necessity multiconfigurational wave functions. The concept becomes meaningless together with Hartree–Fock or DFT wave functions. It is important to emphasize that the NO occupation numbers are stable quantities that do not vary much when a wave function is improved, once a wave function has been defined that includes the most important NOs. The dependence on the AO basis set is also small, which makes the NOs and their occupation numbers very useful as measures of the bonding in a molecule. As many quantities used to describe what the electrons do in a molecule, the bond order is not a measurable quantity, nor is it directly related to such quantities. Different definitions are therefore possible, from a simple count of electrons to more sophisticated measures based on different partitionings of the density matrix. Such measures are, however, often very method- and basis-set-dependent, which is not the case for the definition applied here.

Before 1964, it was assumed that the highest bond order that could exist between two atoms was three. That...
Cotton et al. reported the crystal structure of K₃[Re₂Cl₈]·2H₂O and introduced the idea of a quadruple bond between two transition-metal atoms. The [Re₂Cl₈]²⁻ ion has since become the prototype for this type of complex. A large number of similar compounds that contain a multiply bonded transition-metal dimer have been synthesized. The metals are usually in the +2 oxidation state or higher, and the largest formal bond order is four. However, in 2005 Nguyen et al. synthesized a dichromium compound with the general structure [ArCrCrAr], where Cr is in the +1 oxidation state and Ar is an aryl group. This complex is the first example of such a compound, which has a formal quintuple bond. Only one σ bond and a pair of π bonds are possible for main-group atoms and are formed from the s- and p-type atomic orbitals, while for transition metals two σ bonds, one pair of π bonds, and one pair of δ bonds are possible from the s- and d-type atomic orbitals, thus leading to a maximum possible bond order of six. Multiple bonding also becomes less favored for heavier main-group atoms, while the opposite is true for transition metals, as will be shown below.

Over the years we have studied several metal–metal multiple-bond compounds and recently we have extended this concept to the whole periodic table, including actinides. Here, we shall briefly review the results and draw some general conclusions concerning the possible bond orders that can be achieved. The highest bond order one might expect for a transition-metal dimer is six, involving the five nd orbitals and the (n + 1)s orbital. Six electrons are needed on each atom, so the possible candidates are Cr, Mo, and W and possibly also Mn⁺, Tc⁺, and Re⁺, even if such bonds are not yet known. The chromium diatom has been studied for many years both experimentally and theoretically. The most recent theoretical work yields a diatom with a bond length of 1.66 Å and a bond energy of 1.65 eV, in good agreement with the experimental work yielding a diatom with an equilibrium geometry. This aspect is nicely illustrated by the potential curves in Figure 1. They demonstrate the elusive nature of contracting s- and p-type orbitals while those with higher angular momentum are expanded. As a result, the s and d orbitals in second- and especially third-row transition metals are more equal in size. This greater equivalency in size considerably enhances the bond strength of the corresponding diatoms. Recent theoretical studies, using relativistic multiconfigurational quantum chemical methods, yield a bond energy of 4.41 eV (4.48 eV) for Mo₂ and 5.37 eV (5.17 eV) for W₂ (experimental values are given within parentheses) and bond lengths of 1.95 Å (1.94 Å) and 2.01 Å, respectively. Note the small difference in bond length between Mo₂ and W₂, which illustrates the relativistic contraction in the W₂ molecule. The computed EBO is 5.17 for Mo₂ and 5.19 for W₂, much closer to six than for the chromium diatom. The difference is illustrated in the potential curves in Figure 1. They demonstrate the elusive character of the Cr–Cr bond compared to the more stable Mo and W diatoms.

We have thus arrived at the conclusion that a sextuple bond exists in Mo₂ and in particular in W₂, but hardly in Cr₂. The next issue to address is then: Do even higher bond orders exist? In order to arrive at septuple or higher bond orders, it is necessary to invoke one more shell of atomic orbitals. The f-
type orbitals of the lanthanides and actinides are the only choice for atoms of interest in chemistry. We can immediately exclude the lanthanides; it is well-known that the f orbitals in these elements are more contracted than the valence orbitals, 6s and 5d, and do not participate in any chemical bonds. The situation is different for the actinides, where the 5f orbitals are known to be chemically significant. A recent study of the uranium diatom showed the presence of a quintuple bond\[5\] rather than the expected sextuple bond. The bond (the computed bond energy was only about 1.2 eV) is not strong enough to allow a full promotion of the uranium atoms to the most effective valence state. As a result, some of the 5f electrons remain atomic in character and others exhibit only weak bonding. The computed EBO is 4.2. The diactinide7felectrons remain atomic in character and others exhibit complex bonding, but the EBO is only 3.7. Complexes of the type \[\text{U}_2\text{Cl}_6\] and \[\text{U}_2(\text{OCHO})_6\], formed from two unequal atoms.

The maximum bond order achieved between two atoms in the periodic table is thus six and is represented by the Mo and W diatoms. It remains to be seen if complexes involving the dimer X\(^2\)-Y\(^2\) (X=Mn, Tc, or Re) could exhibit sextuple bonding, but such compounds have neither been synthesized nor studied theoretically. What about quintuple bonds? We have seen above that the elusive diatom \(\text{Pa}_2\) (which will probably never be made) has the most developed quintuple bond among the actinides. Among compounds of the transition metals, \([\text{ArCrCrAr}]\) was found to have a weak quintuple bond with an EBO of only 3.5. Larger values are expected if we replace Cr with Mo or W. Among the transition-metal diatoms, one would look for atoms with a d\(^5\) ground state. The only atom that fulfills this condition is Nb. Preliminary calculations give a strong bond for Nb\(_2\) with EBO > 4.0. The tantalum diatom is another possibility, but the Ta atom has the ground state d\(^5\) and a promotion energy of 1.28 eV is needed to arrive at a valence state with five unpaired electrons. Thus, Nb\(_2\) is most likely to be the best candidate for a strong quintuple bond, or complexes involving Mo\(^3\)-Mo\(^1\) or W\(^3\)-W\(^1\) units.

We have collected the EBO values for the systems discussed above in Table 1. A few general observations can be made. The EBO is always smaller than the maximum formal bond order (MBO); the number of electrons forming the bond divided by two, sometimes much smaller. In such cases it is not very informative to use the MBO to describe the nature of the bond. None of the three dichromium compounds in the table have EBOs close to the MBOs, and the same is true for the uranium compounds and Ac\(_2\). The two values are closer for the other compounds and it is easier to endorse the use of MBO to describe the bonding.

It should also be emphasized that there is no direct correlation between bond order and bond energy. The Cr\(_2[/PhCrCrPh] pair is a nice illustration. The bond energy is a complex quantity that depends on many factors, such as atomic promotion energy and the interplay between attractive nuclear forces and electron repulsion, among other factors. The increased bond energy in Mo\(_2\) and W\(_2\) relative to Cr\(_2[/Cr2(O2CCH3)4]\) can partly be explained by the decreased electron repulsion in the 4d and 5d shells, which are more diffuse than the compact 3d shell. For heavier elements, spin–orbit coupling, which is often quenched in the molecule but large in the atoms, decreases the bond energy. As an example, it reduces \(D_0\) in W\(_2\) by more than 1 eV. Finally, it should be mentioned that the above discussion refers only to the covalent bond between two equal atoms. A more developed measure that also includes electrostatic interactions would have to be developed to deal with ionic bonds between two unequal atoms.

### Computational Details
All computed results discussed in this article have been obtained by using relativistic multiconfigurational quantum chemistry. The Complete Active Space (CAS) method has been used to generate multiconfigurational wave functions that can describe weak bonding and dissociation processes properly.\[10\] Multiconfigurational second-order perturbation theory (CASPT2) has been used to add effects of dynamic electron-correlation effects to structures and energetics.\[12,13\] Relativistic effects have been included by using the Douglas–Kroll–Hess approximation. Scalar relativity has been included at all levels of theory, including the generation of the basis sets. Effects of spin–orbit coupling are treated by a configuration-interaction procedure where the basic states are CASSCF wave functions for electronic states that are close in energy. A detailed account of the procedure is given in reference [14]. Details of the procedure for choosing active orbitals, basis sets, and so on can be found in the respective referenced papers.

### Table 1: Effective bond orders and bond energies for the compounds discussed in the article.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>MBO</th>
<th>EBO</th>
<th>(D_0) [eV]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr(_2)</td>
<td>6</td>
<td>3.5</td>
<td>1.6</td>
</tr>
<tr>
<td>[PhCrCrPh]</td>
<td>5</td>
<td>3.5</td>
<td>3.2</td>
</tr>
<tr>
<td>[Cr(_2/(O2CCH3)4)]</td>
<td>4</td>
<td>2.0</td>
<td>–</td>
</tr>
<tr>
<td>Mo(_2)</td>
<td>6</td>
<td>5.2</td>
<td>4.4</td>
</tr>
<tr>
<td>W(_2)</td>
<td>6</td>
<td>5.2</td>
<td>5.4</td>
</tr>
<tr>
<td>Ac(_2)</td>
<td>3</td>
<td>1.7</td>
<td>1.2</td>
</tr>
<tr>
<td>Th(_2)</td>
<td>4</td>
<td>3.7</td>
<td>3.3</td>
</tr>
<tr>
<td>Pa(_2)</td>
<td>5</td>
<td>4.5</td>
<td>4.0</td>
</tr>
<tr>
<td>U(_2)</td>
<td>6</td>
<td>4.2</td>
<td>1.2</td>
</tr>
<tr>
<td>[PhUUPh]</td>
<td>5</td>
<td>3.7</td>
<td>–</td>
</tr>
<tr>
<td>[Re(_2/Cl] 6)</td>
<td>4</td>
<td>3.2</td>
<td>–</td>
</tr>
</tbody>
</table>

All calculations have been carried out with the quantum chemistry software MOLCAS.[11]

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