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Metal–Metal Multiple Bonds

Reaching the Maximum Multiplicity of the Covalent Chemical Bond**

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The bond order and in particular the possibility of multiple bonding between atoms in a molecule have been highlighted in two recent articles.[1,2] Theoretical and experimental work have challenged old chemical paradigms concerning the possible multiplicity that can be achieved in a chemical bond. On the other hand, the concept of a multiple bond is not clearly defined and there is a need for a more quantitative measure. In this contribution we attempt to introduce such a measure and apply it to a number of multiply bonded systems. As a result of the analysis, we show that the highest multiplicity that can be achieved in a bond between two equal atoms is six. The multiplicity of a chemical bond is determined by the number of electron pairs that occupy the region between the two bonded atoms in bonding molecular orbitals. The hydrogen molecule has, for example, a single bond with two electrons in one orbital formed from the 1s orbitals on each atom. The nitrogen molecule, N_2, has a triple bond; the three unpaired 2p electrons on each atom combine to form this very strong bond. Before 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. The maximum value is reached by the tungsten diatom, W_2. No other pair of atoms in the periodic system (atomic numbers smaller than about 100) reaches a higher bond order.

A single covalent chemical bond between two atoms is, in simple molecular orbital (MO) theory, described by a bonding orbital occupied by two electrons. This is, however, an oversimplified picture of bonding that only works for strong bonds and near the equilibrium geometry. None would say that there is a chemical bond between two hydrogen atoms that are at a distance of 100 Å from each other. However, this is the picture that emerges from the simple theory. A more accurate description uses two orbitals to describe the bond: a bonding orbital and the corresponding antibonding orbital. Both orbitals are occupied in the true wave function of the molecule. Let us assume that the occupation of the bonding orbital is $\eta_b = 2-x$. The occupation of the antibonding orbital will then be close to $\eta_a = x$, such that the sum is two. When the molecule is close to equilibrium, x will be small for a normal chemical bond, but when the molecule dissociates, x will increase to become one. In this case, there is no chemical bond and the wave function describes a system of two radicals with one electron on each of them. We can use this property of the molecular orbitals to define an *effective* bond order (EBO) for a single bond as $(\eta_b-\eta_a)/2$, which is then close to one for a normal chemical bond but goes to zero when the bond weakens. For multiply bonded molecules we add up the contributions from each bond to obtain the total EBO. The EBO is non-integer and in naming the multiplicity of a bond one may then use the lowest integer value larger than the EBO.

Why is this interesting? If one assumes that the bond formed between the two fragments is weak for some reason, 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 $1-x = 0.5$. 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

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year Cotton et al. reported the crystal structure of $K_2[Re_2Cl_8]\cdot 2H_2O$ and introduced the idea of a quadruple bond between two transition-metal atoms.[3] The $[Re_2Cl_8]^{2-}$ ion has since then 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.[4] 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 values (see reference [5] for further details and references). Let us take a closer look at the electronic structure of this molecule. Twelve orbitals are used to describe the bonds, the five 3d orbitals and the 4s orbital on each atom. The calculated occupation of the bonding orbitals are: $4s\sigma_g$ 1.90, $3d\sigma_g$ 1.77, $3d\pi_u$ 3.62, $3d\delta_g$ 3.16; and those of the antibonding orbitals are: $4s\sigma_u$ 0.10, $3d\sigma_u$ 0.23, $3d\pi_g$ 0.38, $3d\delta_u$ 0.84 (note that π and δ describe a pair of degenerate orbitals with a maximum possible occupation of four electrons). The EBO that was computed from these numbers is 3.52, which is far from the possible limit of six. The reason for this deviation is the weak interaction between the $3d\delta$ orbitals, which can be described as an intermediate between a chemical bond and four antiferromagnetically coupled electrons. The chromium diatom could thus also be described as a quadruply bonded system with the δ electrons localized on the separate atoms and coupled to a total spin of zero. This behavior is typical for the interaction between first-row transition-metal atoms. Another example is the complex [ArCrCrAr] synthesized by Nguyen et al.[4] A model complex of this molecule, in which the large Ar groups were replaced by phenyl groups, has recently been studied using multiconfigurational quantum chemistry.[6] The computed EBO was 3.52, considerably lower than five. Again, the low value is due to the weak coupling of the δ orbitals. The dichromium(II) complex $[Cr_2(O_2CCH_3)_4]$ has a formal bond order of four, but the EBO is only 1.99, thus showing the weakness of the four 3d bonds, in particular the single $3d\delta$ bond.[7] Here the bond order is further diminished by the repulsive interaction of the two positively charged ions.

One reason for the weakness of the Cr–Cr bond is the difference in size between the 3d and 4s orbitals. The much larger 4s orbital generates a 4s–4s bond with a considerably longer bond length than the 3d–3d bonds. This unbalance weakens the 3d bonds and makes the 4s bond repulsive at equilibrium geometry. This aspect is nicely illustrated by the bond energy, which is only 1.66 eV for Cr_2 but 3.17 eV for [PhCrCrPh], thus showing that there is no direct relation between bond order and bond energy. Another contributing factor is the repulsive interaction between the closed 3p shells, which have about the same radial extension as the 3d orbitals.

The unbalance between the s and d orbitals decreases for the second-row transition metals and even more for the third row. Relativistic effects play an important role in making the two sets of orbitals more equal in size. Relativity has the effect 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 Mo_2 and 5.37 eV (5 ± 1 eV) for W_2 (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 Mo_2 and W_2, which illustrates the relativistic contraction in the W_2 molecule. The computed EBO is 5.17 for Mo_2 and 5.19 for W_2, 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 Mo_2 and in particular in W_2, but hardly in Cr_2. 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-

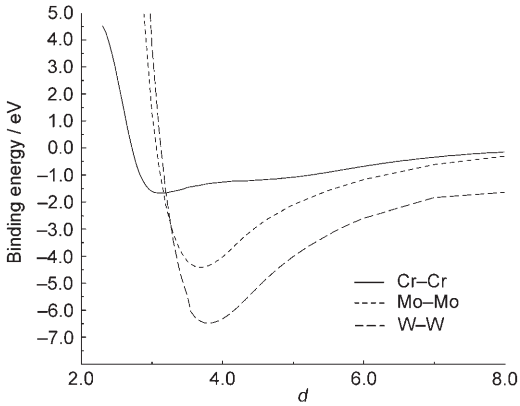

Figure 1. Potential curves for the dimers Cr_2, Mo_2, and W_2; $d=$ internuclear distance in atomic units.

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 other 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,[8] 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 diactinides Ac_2, Th_2, and Pa_2 have also been studied.[16] Ac_2 has a double bond (EBO = 1.7), Th_2 a quadruple bond (EBO = 3.7), and Pa_2 a quintuple bond (EBO = 4.5). With the Pa_2 diatom we have reached the maximum bonding power among the actinide diatoms. In U_2 the bond energy decreases and the bond length increases. This effect is due to the increased stabilization of the 5f orbitals and the corresponding destabilization of the 6d orbitals. The trend will most certainly continue for the heavier diactinides, and we can thus without further calculations conclude that Pa_2 is the most strongly bound actinide diatom with its fully developed quintuple bond with an EBO not much smaller than five. No diatoms with bond orders larger than six exist in the actinide series and thus nowhere in the periodic table (atomic numbers less than about 100). A number of diuranium complexes have also been studied even though experimental evidence for the existence of such compounds do not yet exist. The diuranium counterpart of the [PhCrCrPh] complex, [PhUUPh], has recently been reported.[9] Formally, a quintuple bond could be formed between the two U^I units, but the EBO is only 3.7. Complexes of the type $[U_2Cl_6]$ and $[U_2(OCHO)_6]$, formed from two U^{III} units exhibit weak U–U triple bonds.[10]

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^I–X^I (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 Pa_2 (which will probably never be made) has the most developed quintuple bond among the actinides. Among compounds of the transition metals, [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^4s^1 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^3s^2 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^I–Mo^I or W^I–W^I 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.

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

Molecule	MBO	EBO	D_0 [eV]
Cr_2	6	3.5	1.6
[PhCrCrPh]	5	3.5	3.2
$[Cr_2(O_2CCH_3)_4]$	4	2.0	–
Mo_2	6	5.2	4.4
W_2	6	5.2	5.4
Ac_2	3	1.7	1.2
Th_2	4	3.7	3.3
Pa_2	5	4.5	4.0
U_2	6	4.2	1.2
[PhUUPh]	5	3.7	–
$[Re_2Cl_8]^{2-}$	4	3.2	–

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 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.[11] 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.

All calculations have been carried out with the quantum chemistry software MOLCAS.[15]

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