# Transition Metals Compounds: Outstanding Challenges for Multiconfigurational Methods

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**ABSTRACT:** The present contribution provides a "perspective" on the work on transition metal (TM) bonding and spectroscopy by Björn O. Roos, performed by means of the CASPT2 method in the period 1992–2010. After giving a short overview of important nondynamic correlation effects appearing in TM atoms and molecules, ample attention is given to the work on the $Cr_2$ molecule and to Björn's fascination for multiple bonds in inorganic molecules containing TM. A short description is also given of his contributions to bioinorganic chemistry, with emphasis on the blue copper proteins.   © 2011 Wiley Periodicals, Inc. Int J Quantum Chem 111: 3291–3301, 2011

**Key words:** ab initio quantum chemistry; multiconfigurational methods; transition metal complexes; multiply bonded metal dimers; blue copper proteins.

## 1. Introduction

In this article, an overview of some important achievements of Björn Roos in the field of computational transition metal (TM) chemistry is given. The overview essentially starts in 1992, the year when the CASPT2 method [1, 2] (second-order perturbation theory based on a complete active space SCF wave function) was implemented into the MOL-CAS software, developed in Roos' group at the University of Lund (Sweden) [3, 4]. Before this time, several studies on small molecules such as NiH [5], $Ni(C_2H_4)$ [6], MCO (M = Fe, Ni, Cu) [7, 8], $CuX_2$

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(X = F, Cl) [9], and a first CASSCF study on $Cr_2$ [10] are of course also worth mentioning. These studies were performed at the CASSCF or (limited) CI level. Even though each of them was a must read for every researcher attempting to use correlated ab initio methods to describe TM systems, they in fact only presented small steps in a field that at the time was largely unexplored, mainly because of computational limitations. Undoubtedly, the introduction of CASPT2 into this domain was revolutionary. From one day to the next it became possible to study the bonding and electronic spectra of "genuine" TM complexes such as $Cr(CO)_6$ [11] and ferrocene [12], leaving behind the strict limitations on the size of the reference wave function and on the total number of correlated electrons that used to jeopardize both the size of the system and the accuracy to be obtained

from a CI treatment. What was needed though was a thorough knowledge of the character and the importance of possible nondynamic correlation effects in the systems under study. Indeed, as these correlation effects cannot be handled properly in the second, perturbational step of the calculation, including them in the first, CASSCF step is a prerequisite for obtaining accurate CASPT2 results. Over the years, hardware developments and improvements in the MOLCAS software have stretched the limits of the the active space used to build the CASSCF wave function from 10–12 to 15–17 orbitals. As we will show in section 2, this is sufficient to describe the ground state electronic structure of most TM systems, providing CASPT2 results with an accuracy (0.02 Å for interatomic distances and 0.3 eV for relative energies) that is comparable with what can be expected for more standard organic molecules [13].

## 2. Nondynamic Correlation Effects in TM Complexes: The "Basic Ten" and the "Double-Shell Effect"

The very first application of CASPT2 in TM chemistry concerned the spectrum of the nickel atom [14]. This atomic case was chosen because of its reputation of being extremely hard to treat with ab initio methods. The ground state of the nickel atom is $d^9s^1(^3D)$, with a very close-lying $d^8s^2(^3F)$ state at 0.03 eV (averaged over the $j$ manifold). However, at the numerical Hartree-Fock (HF) level, the latter state is calculated as much as 1.63 eV below the $^3D$ ground state (including relativistic effects). An even larger error is obtained for the lowest $d^{10}(^1S)$ state, calculated 4.33 eV above $^3D$ with numerical HF, 2.49 eV higher than the experimental excitation energy of 1.74 eV.

CASPT2 calculations on the nickel atom were performed with extended ANO-type basis functions, uncontracted in the core-valence region to provide an accurate description of (3s3p) correlation effects, and several active spaces were tested, the largest space consisting of 10 electrons in 14 orbitals (3d,4s,4p,3d'). The results obtained from this ambitious set of calculations were surprisingly accurate. After including relativistic effects (taken from numerical HF calculations [15]), a maximum deviation of 0.1 eV was obtained. This certainly was a promising start for CASPT2 in TM chemistry. However, the most important conclusion was that to reach this type of accuracy including in the active

space a second 3d' shell is indispensible. The 3d double-shell effect was born, and its importance would later prove to be systematic in all studies on complexes containing a first-row TM with a more-than-half filled 3d-shell, in particular when considering electronic transitions involving a change of the 3d occupation number, for example, 3d → 4s or charge-transfer excitations. The importance of the nd double-shell effect is, however, drastically reduced, when going to the second and third TM series [16].

A next important question concerning the use of CASPT2 in TM chemistry was then of course how to construct the active space for TM complexes containing more than one or two ligands. With an increasing number of ligands, it obviously becomes impossible to include all valence orbitals in the active space, so a rational choice has to be made. A satisfactory answer to this problem was found in three studies on the bonding and spectroscopy of different organometallic systems, that is, the TM carbonyls $Ni(CO)_4$, $Fe(CO)_5$, $Cr(CO)_6$ [11], $Ni(C_2H_4)$ and ferrocene [12], and a series of hexacyanometallate complexes of first-row TM ions [17]. Important correlation effects were found to be connected to the formation of covalent bonds between the metal 3d-orbitals and the ligands, either involving $\sigma$- or $\pi$-donation of an electron pair from the ligands into the (formally empty) metal 3d orbitals, or $\pi$-backdonation from a doubly occupied d-orbitals into a ligand $\pi^*$ orbital. Such correlation effects would have to be accounted for in the CASSCF wave function by including in the active space both the bonding and antibonding metal d-ligand valence combinations involved in the covalent bond(s). In essence it means that all molecular orbitals containing a significant metal d contribution should be active. With five d-orbitals, this then, in practice, gives an active space of ten orbitals. It was also found that, for example, in case of $d^{10}$ $Ni(CO)_4$ the correlating shell, quite conveniently, contains a mixture of CO $\pi^*$ and 3d' character, such that it serves to describe both the double-shell effect and the correlation effects connected to Ni-to-CO $\pi$-backdonation.

Remaining correlation effects were dealt with in the second, CASPT2, step. Based on an active space of 10 orbitals, ground state structures and binding energies were calculated in close agreement with the available experimental data, with deviations of less than 0.02 Å for metal–ligand distances and less than 5 kcal/mol for (total) binding energies. A similar accuracy was also obtained for excited states: the ligand field spectra of hexacyanometallate complexes could be reproduced with an accuracy, 0.3 eV, that

was unprecedented in ab initio quantum chemistry for molecules (containing TM) of this size.

As a critical note, it should be mentioned that the good results obtained from CASPT2 for the binding energies for these organometallic systems may have been the result of a fortunate cancellation of errors, mainly related to limitations of the ANO-s basis sets used in these studies. The ANO-s library was constructed in 1995 [18], aiming at providing a systematic series of moderately sized ANO-type basis sets for all elements H–Kr, thus making it possible to perform reasonably accurate correlated calculations on large systems such as ferrocene. However, a major drawback of the ANO-s basis sets for the TM was that inclusion of metal (3s3p) correlation was not considered in the construction of the contracted sets. Semicore (3s3p) correlation was shown to have a considerable influence both on the relative energies of different low-lying states in TM atoms and ions [14, 19] as well as on the binding energies of their complexes [11, 12]. However, because the appropriate basis functions for the description of this type of correlation were lacking from the ANO-s (and also the ANO-l [20]) basis sets, including (3s3p) correlation would lead to huge basis set superposition errors (BSSE) on the binding energies, in the order of 30 kcal/mol or more. These errors were corrected for by means of a (standard) counterpoise method, however giving corrections that were afflicted with quite large error bars. Together with the somewhat preliminary description of relativistic (Darwin and mass-velocity) effects, this makes that the accuracy of the computed binding energies should be looked at in their proper perspective. Both relativistic (Douglas–Kroll–Hess) and semicore correlation effects were included in the construction of the recently developed ANO-rcc basis sets for the TM [21], which should therefore be capable of providing much more accurate CASPT2 binding energies for these prototype organometallic systems.

## 3. The Cr–Cr Bond: A Golden Wire through the Career of Björn Roos

Any introductory course on multiconfigurational methods almost as a rule starts from the dissociation problem of the $H_2$ molecule [22]. Making use of a molecular orbital (MO) picture, students are taught that, whereas at the equilibrium distance the H–H single bond in this molecule may be adequately described by a closed-shell HF configuration $\sigma_g^2$, with $\sigma_g$ the bonding MO combination of the 1s orbitals

on both H, occupation of the antibonding $\sigma_u$ MO needs to be invoked to describe the bonds at a longer distance, leading to proper dissociation. The course might further continue by extending this concept to $N_2$, where six orbitals are needed to describe the dissociation of a formally triple bond. If the course is taught by Björn Roos, the story would certainly be finalized with an introduction to the $Cr_2$ molecule, as the "golden case" for multiconfigurational ab initio quantum chemistry. Indeed, in its $^7S$ ground state, each chromium atom possesses five unpaired 3d and one 4s electron and can therefore, in principle, afford to form a fully sextuple bond. In reality, however, due to several weakening factors (cfr section 4) the effective bond order (EBO) of the Cr–Cr bond is closer to four than to six. As such, it should come as no surprise that the ground state of $Cr_2$ is highly multiconfigurational in character. This is demonstrated by the weight of the closed-shell HF configuration in the total wave function, which is only 45% at the equilibrium geometry [23].

With a Cr–Cr quadruple bond, one would still expect a strongly bonded dichromium system. This expectation is corroborated by the experimentally observed short Cr–Cr distance, only 1.68 Å [24]. On the other hand, the corresponding bond energy $D_0$ of 1.53 (±0.06) eV [25], rather points a much weaker bond. This weakness of the Cr–Cr bond is caused by two important factors [26]. The most important factor is the difference in size between the 3d and 4s orbitals. The much larger 4s orbital generates a 4s–4s bond with a much longer bond length than the 3d–3d bond. This 4s–4s bond is in fact manifested by a shoulder at a longer Cr–Cr separation around 3.0–4.0 Å in the experimental potential energy curve [27]. Another weakening contribution is due to the closed 3p shells, which have about the same radial extension as the 3d orbitals. This gives rise to a repulsive interaction between both shells at the equilibrium distance, thus further decreasing the Cr–Cr binding energy.

Over the years, a multitude of theoretical efforts, both with conventional correlated methods and with density functional theory (DFT), have been devoted to the understanding and quantitative description of the Cr–Cr bond. For an overview, we would like to refer to a recent review article by Brynda et al. [28] and references therein. A first CASSCF study with 3d and 4s active and including 12 electrons was already presented in 1983 [10]. It was found that CASSCF is not capable of providing a qualitative correct description of the wave function at all bond distances, leading to an unbound molecule. Clearly, the

dynamic correlation effects are too large. A method was needed that can account for such effects on top of a very large reference wave function. The (12in12) CASSCF wave function comprises 28,784 configuration state functions (CSFs), obviously too much to serve as the reference for a traditional multireference configuration interaction (MRCI) treatment. In 1999, an MRACPF calculation was presented by Dachsel et al. [29], based on a reduced (to 3088 CSFs) reference wave function. The CI calculation comprised almost 1.3 billion configurations and was presented as a "tour de force," involving massively parallel computations. The binding energy resulting from this calculation was still 0.4 eV too low. This error was attributed to limitations in the one-particle basis set and the lack of relativistic effects. This CI study was presented a few years after the development [1, 2] and application to $Cr_2$ [30] of the CASPT2 method, which allowed to treat dynamic correlation in a robust way, starting from the full CAS wave function, by replacing the time-consuming CI by a second-order perturbational treatment. However, even though already providing a reasonable description of the potential energy curve, the first CASPT2 calculation of $Cr_2$ was afflicted by a number of severe problems, related both to the formulation of the CASPT2 method (i.e., the zeroth-order Hamiltonian), the one-particle basis set and the description of relativistic effects. Over the years, solid solutions for these problems were implemented in the MOLCAS software, and most often $Cr_2$ was used as a primary test case for improvements in the methodology. In fact, looking back today at the determination and systematics with which different solutions were proposed and implemented one cannot avoid wondering whether the $Cr_2$ problem did not in fact (in the back of Björn's mind) play a determining role as a driving force for such improvements.

In the first CASPT2 calculations on $Cr_2$, a large number of intruder states appeared, giving rise to quite a number of singularities along the potential energy curve [30]. In 1995, a level shift technique was introduced [31], which made it possible to remove the intruder states from the first-order wave function and to produce stable second-order energies and smooth potential curves. Some time later Forsberg and Malmqvist presented an alternative, very effective way of dealing with the singularities, replacing them by a small distortion of the potential function, called the imaginary denominator shift [32]. Again, the potential curve for $Cr_2$ was used as an illustration. Another problem with the description of the $Cr_2$ potential energy curve was due to the

original formulation of the zeroth-order Hamiltonian $\hat{H}^{(0)}$ in CASPT2, which would systematically favor high spin over low spin states [13, 33]. A first remedy was formulated by Kerstin Andersson in the so-called $g1$, $g2$, and $g3$ modifications of $\hat{H}^{(0)}$. Using such modified forms of the zeroth-order Hamiltonian a detailed description of a large number of $Cr_2$ excited states could be provided [34]. Later the IPEA modified $\hat{H}^{(0)}$ was introduced [35] and became the standard zeroth-order Hamiltonian in MOLCAS 6.4. Once the problems with the CASPT2 methodology itself were dealt with, remaining sources of error in the description of the $Cr_2$ potential curve were due to the incapability of the available ANO basis sets of properly describing semicore (3s3p) correlation (giving rise to large BSSE) and to the approximate treatment of relativistic effects. The first problem was solved by the development of the ANO-rcc series of basis sets for the TM [21] (and for the rest of the periodic system), while the combination of CASSCF with relativistic quantum chemistry [36] (in terms of the Douglas–Kroll–Hess ansatz and including spin-orbit coupling [37]) made it possible to improve also this aspect of the computation.

In 2003, just after his retirement, Björn Roos presented his final CASPT2 calculations on the chromium dimer [23]. The computed bond distance is 0.017 Å shorter than the experimental value, whereas the computed value for $D_0$ is 1.65 eV, 0.12 eV larger than experiment. Up to a distance of 2.7 Å, the shape of the dissociation curve obtained from CASPT2 is virtually indistinguishable from the RKR (Rydberg–Klein–Reese) curve, deduced from the experimental vibrational frequencies [27]. At higher distance, both curves start to deviate somewhat. It was suggested that this might be due to deficiencies in the RKR potential rather than to inadequacies in the theoretical treatment.

Obtaining an accurate CASPT2 description for the $Cr_2$ dissociation curve, however, did not mean the end of Björn Roos' activity on the dichromium dimer. On the contrary, as we shall see in the next section, it rather marked the beginning of a very active research period on molecular systems involving this dimer as well as its second- and third-row analogs $Mo_2$ and $W_2$.

## 4. Recent Studies on Multiply Bonded TM Systems

With six available electrons in the $n$d and $(n + 1)$s orbitals, the bare dimers of the group six B

elements $Cr_2$, $Mo_2$, and $W_2$, potentially provide the most extreme example of multiple bonding between two TM. However, these molecules have no stable existence at room temperature, making them of limited relevance to inorganic chemists. A great challenge for synthetic work in this field is rather to stabilize multiply bonded metal–metal species by providing them with appropiate ligands, either coordinated terminally or as a bridge between the two metals. However, each ligand that is introduced also reduces the possibility for multiple metal–metal bonding, because those metal valence orbitals that become involved in the metal–ligand interaction are no longer available for bonding with the neighboring metal. The search for the highest possible multiplicity of the metal–metal bond got its first success in 1965, with the synthesis by Cotton and Harris [38] of the room temperature stable $Re_2Cl_8^{2-}$ species with a formal quadruple bond. Since then, a large number of similar compounds that contain a multiply bonded TM dimer were synthesized and theoretically studied, among which many low-valent chromium–chromium compounds [39]. However, until 2005 the maximum bond multiplicity of four was never exceeded in any of these compounds, and $Re_2Cl_8^{2-}$ therefore remained the prototype of multiply bonded metal dimers.

Only 5 years ago Nguyen et al. [40] succeeded in synthesizing for the first time a stable Cr–Cr complex, [ArCrCrAr] ($Ar' = C_6H_3-2,6(C_6H_3-2,6-Pr_2^i)_2$), in which two chromium ions appear as Cr(I) $d^5$, thus sharing five electron pairs in a (formally) fivefold bond, with a distance of 1.835 Å. This discovery marked a new milestone in the experimental research on multiply bonded TM complexes and was the start of a very productive period in the synthesis of other low-valent chromium–chromium complexes [41–45], all aiming at reaching the shortest possible bimetallic distance in coordination compounds. These experimental studies were accompanied by a number of theoretical studies, aiming at characterizing the extent of multiple bonding in the experimentally reported Cr–Cr cores.

It also gave an additional boost to Björn's work on dimetallic systems, resulting in a series of publications in highly cited journals [26, 46, 47]. The methodology and basis sets were at this time available in MOLCAS to obtain accurate CASPT2 numbers for structures, bond strengths, and relative energies. However, although such numbers are presented in the articles, this recent work was primarily focused on providing conceptual insight into the multiconfigurational nature of the metal–metal bonds in the

experimentally reported complexes. To this end a quantity named EBO was defined, which quantifies the extent of multiple bonding obtained from (reflected by) a CASSCF wave function [26].

Bond order is a concept that stems from molecular orbital theory, where it is defined as half the difference between the total number of electrons occupying the bonding molecular orbitals and the total number of electrons occupying the corresponding antibonding orbitals. Without considering correlation, these occupation numbers are integers and so is the bond order. For example, in the HF ground state wave function of $Cr_2$, six unpaired electrons originating from (3d, 4s) couple into six bonding molecular orbitals, leaving the corresponding antibonding orbitals empty. This then gives a bond order six. On the other hand, in in the [ArCrCrAr] dimer synthesized by Nguyen, [40] the Cr–Cr bond order is diminished to five, because one of the unpaired electrons on each side is now used for Cr–Ar bond formation, leaving only 10 electrons to gather in five bonding molecular orbitals of $\sigma$-, $\pi$-, and $\delta$-type. (The latter two each describing a pair of degenerate orbitals). Similarly, the Re–Re bond in Cotton's $Re_2Cl_8^{2-}$ complex is most conveniently described as built from two Re(III) $5d^4$ ions, ionically coordinated by four $Cl^-$ ions each, and each providing four electrons to one $\sigma$, two $\pi$, and one $\delta$-type bonding molecular orbital, thus giving a bond order four.

The bond order defined as such is conveniently used among inorganic chemists, forming the basis for the description of the bond multiplicities in all publications reporting the synthesis of TM dimer complexes. Even if the authors of these articles may be aware that this is in fact an oversimplified picture of bonding that only works for strong bonds, a more quantitative measure of bond multiplicity cannot be provided by any single-configurational molecular orbital description of the ground state. However, when allowing instead a multiconfigurational description using a CASSCF wave function, the definition of bond order may in a straightforward way be extended to give the following EBO $= (\eta_b - \eta_a)/2$, $\eta_b$ and $\eta_a$ now representing the occupation numbers of the natural orbitals obtained after diagonalization of the first-order density matrix. The CASSCF calculation should have an active space consisting of (at least) the bonding and antibonding molecular orbitals describing the metal–metal bond, $\eta_b$ and $\eta_a$ then are noninteger numbers with $1 \leq \eta_b \leq 2$ and $0 \leq \eta_a \leq 1$, adding up to two for each specific bond. In the limit of a very strong bond, $\eta_b$ is two whereas $\eta_a$ is zero, thus giving an

EBO = 1. However, weak bonds have an occupation number $\eta_b$ that strongly deviates from two, and vice versa for $\eta_a$. In the limit that both occupation numbers approach one, true bond formation has been replaced by antiferromagnetic coupling between the two electrons. Such a situation occurs for example for the $\delta$ bonds in $Cr_2$. Twelve orbitals are used to describe the bonds in this molecule. The calculated occupation of the bonding orbitals are: $4s\sigma_g$ 1.90, $3d\sigma_g$ 1.77, $3d\pi_u$ 1.81, $3d\delta_g$ 1.58, and those of the antibonding orbitals are: $4s\sigma_u$ 0.10, $3d\sigma_u$ 0.23, $3d\pi_g$ 0.19, $3d\delta_u$ 0.42. This gives an EBO of 0.90 for the 4s $\sigma$, 0.77 for the 3d $\sigma$ bond, whereas for each of the two 3d $\pi$ and 3d $\delta$ bonds an EBO of, respectively, 0.81 and 0.58 are found. The total EBO computed from these numbers is 4.45, significantly smaller than the possible limit of six, and the main reason for the 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. In this way, the EBO does not only provide a quantitative measure of the actual rather than the formal bond multiplicity but also points to the presence of weak bond components, which may be associated in an intuitive manner with possible reactivity with external compounds or with the supporting ligands themselves [48].

The presence of weak $\delta$ bonds is typical for TM dimers. It was also found in a CASSCF/CASPT2 study of the complex [ArCrCrAr] synthesized by Nguyen et al. [40]. Both for this complex and for a model complex with the large Ar groups replaced by phenyl groups [47], the computed EBO, 3.43–3.52, is far lower than the quintuple multiplicity that is commonly assigned to this bond. In another recently reported dichromium complex the Cr—Cr core is coordinated by two bridging diazadiene ligands, giving rise to a trigonal coordination environment around each Cr consisting of two N atoms and the neighboring Cr atom [41]. This again gives a Cr(I)—Cr(I) system with a formally quintuple bond. Interestingly, however, the Cr—Cr bond distance in this complex is only 1.803 Å, shorter by ∼0.03 Å than in the former [ArCrCrAr] complex. Yet the calculated EBOs of both complexes are very similar, around 3.5. This obvious lack of correlation between bond order and bond distance is explained by a different electronic structure of the formally Cr(I) ions in both complexes [49]. In the [ArCrCrAr] both Cr essentially use one of their electrons to form the Cr—Ar $\sigma$ bond. On the other hand, in the diazadiene complex, one of the chromium $\delta$ orbitals becomes intensively involved in $\pi$-backdonation with the

imine-containing ligands, thus partly loosing interest in Cr—Cr $\delta$ bond formation. Most recently [48] a CASPT2 study of a series of other bridged Cr—Cr complexes was reported, in which the diazadiene ligand is replaced by other N-donor containing bridging ligands (amidinate, aminopyridinate, guanidinate), giving rise to a similar electronic structure. Within this series of compounds belonging to the same class of supporting ligands, a linear correlation is found between the bond order and bond length, the latter, however, being dictated primarily by structural constraints imposed by the ligands on the Cr—Cr core. The most effective ligand in producing an extremely short Cr—Cr distances is guanidinate: 1.73 Å, the shortest metal–metal distance observed to date [45] (apart from the bare $Cr_2$ molecule with a Cr—Cr bond length of 1.68 Å). However, most important, even for such short intermetallic distances, the associated EBO of the Cr—Cr bond never exceeds a value of 4.

The question then naturally arises: what is the maximum multiplicity of the chemical bond? This question was adressed in Ref. 26. Within the TM series, the maximum number of unpaired electrons in the $n$d, $(n+1)$s shells is six. This is, therefore, also the maximum bond multiplicity within this series, which can be reached only for the group VIB metals (and possibly the monocations of VIIB). Excluding $Cr_2$ with its EBO of only 4.46, $Mo_2$ and $W_2$ still remain promising candidates. Indeed, the most important bond weakening factors in $Cr_2$, the difference in size between the 3d and 4s orbitals (making the 4s bond repulsive at the equilibrium geometry) and the similar size of 3p, 3d (giving rise to a repulsive (3p,3d) interaction) become much less important in $Mo_2$ and even less in $W_2$. An important role is played by relativistic effects. Relativistic contraction of the $(n+1)$s- and np-shells and concomitant dilatation of the $nd$-shell makes the bonding in these two molecules much more balanced than in $Cr_2$, thus giving rise to much stronger bonds, with bond energies 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), when compared with only 1.65 eV (1.53±0.06 eV) for $Cr_2$. Analysis of the natural orbitals gives an EBO of 5.17 for both $Mo_2$ and $W_2$, again much higher than the $Cr_2$ value. Providing that in naming the multiplicity of a bond one may then use the lowest integer value larger than the EBO, a sextuple bond exists in $Mo_2$ and in $W_2$, but not in $Cr_2$. For even higher bond orders, one has to go beyond the TM and invoke an f-shell. The lanthanides may be ruled out, because the 4f-shell is screened from its environment by the 6s-

and 5d-shells, and hardly participates in any chemical bond. In one of his last lectures, presented in Crete on October 19, 2006, Björn Roos effectively ruled out the possibility of a higher than quintuple bond between any two (equal) actinides, by presenting a detailed analysis of such bonds in all low-lying states of the early actinide dimers $Ac_2$, $Th_2$, $Pa_2$, and $U_2$, and extending the observations to the heavier actinides. This lead to the following timeless conclusion: The maximum bond order achieved between two atoms in the periodic table is six and is represented by the Mo and W diatoms.

## 5. Applications in Bioinorganic Chemistry

Computational bioinorganic chemistry is a field that started to flourish in the beginning of the nineties, with the rise of density functional theory. At that time, CASPT2 applications in TM chemistry were still in an explorative phase. Within a period of just a few years, the low computational cost and (sometimes misleading) accuracy of density functional methods created an explosive activity in DFT applications to problems of biochemical interest involving TM, leaving little or no space for conventional correlated methods. To many bioinorganic chemists quantum chemical methods became synonymous with density functional methods [50–53]. This is therefore without any doubt the field where CASPT2 has had to put in the greatest effort to even keep the door ajar. However, a few great successes were certainly scored in problems involving electronically excited states, where CASPT2 is obviously superior to time-dependent DFT [54]. Only recently, when it became clear that DFT in fact suffers from a few systematic deficiencies when applied to problems involving TMs [51, 55–58], the CASPT2 method was "recovered" as a viable alternative [59, 60].

A first breakthrough of CASPT2 in biochemistry was attained in 1996, with an extensive theoretical study of the blue copper proteins. In this work, DFT and CASPT2 were used hand in hand to provide new important insights into the geometrical and electronic structure and the spectroscopic features of these enzymes. The study was initiated by Ulf Ryde, who got intrigued by the long-standing "enduced rack" or "entatic state" theories explaining enzyme reactivity in general, and the redox properties of blue copper proteins in particular [61–64]. According to this theory, the tertiary protein structure forces the oxidized Cu(II) form of these proteins into a geometry similar to the one preferred by the reduced Cu(I) form, thus, accounting for a small reorganization energy accompanying reduction and, hence, to a high rate of electron transfer [65].

However, DFT structure calculations on different realistic vacuum models of the Cu(II) surrounding in plastocyanin, a typical blue copper protein (involved in photosynthesis), all gave structures that are quite close to the crystal structure of the oxidised form of this protein [66]. In plastocyanin, a single copper ion (with oxidation state varying between I and II) is four-coordinated by the thiolate S of a cysteine residue, two $N^\delta$ atoms of histidine residues and a methionine thioether group. In the oxidized form, the Cu(II) ligand surrounding is trigonal, with the two histidine-N and the cysteine-S (at an unusually short distance) forming the trigonal plane, and the methionine-S bound in an axial position at a large distance. Such a trigonal structure is quite peculiar for Cu(II): four-coordinated inorganic complexes of this ion are almost invariably square-planar. On the other hand, it is close to the (distorted) tetrahedral surrounding found for the reduced Cu(I) form of the same protein, hence the idea that the trigonal Cu(II) structure is in fact enforced by protein strain to reduce the reorganization energy accompanying reduction. In the largest model used in the DFT calculations, cysteine was modeled by an $SCH_3^-$ ligand, methionine by $S(CH_3)_2$ and histidine by imidazole. No protein environment was present, still the optimized structure of this $Cu(imidazole)_2(SCH_3)(S(CH_3)_2)^+$ complex was obviously trigonal, and in fact virtually identical to the crystal structure of plastocyanin. This simple but sensational result ruled out any possibility of strain, and, as formulated by the founder of the induced-rack theory, Malmström: "forced a complete reorientation of the thinking about blue copper proteins." [67].

Two important questions immediately arose: (a) why does Cu(II) in the blue copper proteins prefer a trigonal rather than a tetragonal coordination environment; (b) how can the low reorganization energy be explained, if not by protein strain. These questions were addressed by studying the structures and reorganization energies of a series of small copper complexes in which the ligands are systematically varied [68, 69]. From these studies, it was concluded that not the protein environment, but rather the proper choice of ligands is reponsible for the extraordinary properties of blue copper proteins. In particular, the softness of the methionine and

cysteine ligands plays a crucial role. Soft ligands give rise to both a flattening of the potential energy surface for twisting between a tetragonal and trigonal structure and to oxidized structures that are quite close to a tetrahedron (rather than tetragonal). Furthermore, the large and soft cysteine thiolate group forms a strongly covalent bond to the copper ion, in which charge is transferred from the thiolate group to the Cu(II) ion, thus bringing the effective charge on this metal closer to Cu(I).

The special role played by the cysteine and methionine ligands was further analyzed and diversified in a series of CASPT2 studies of the electronic structure and spectrum of a variety of blue copper proteins, that is, plastocyanin, cucumber basic protein, pseudoazurin, nitrite reductase, and stellacyanin [70–72]. The first four of these proteins are characterized by the same copper ligands of two histidines, cysteine, and methionine, whereas in stellacyanin the methionine ligand is replaced by glutamine. However, distinct differences are found in the structures, electronic spectrum, and ESR characteristics of these different proteins. Within the series plastocyanin—cucumber basic protein—pseudoazurin—nitrite reductase, X-ray diffraction data display a distinct flattening of the structure, together with a lengthening of the copper–cysteine bond and concomitant shortening of the copper–methionine bond. At the same time, a gradual change is observed in the signals obtained from ESR: from an axial spectrum in plastocyanin to a gradually more rhombic spectrum in the other three proteins. The most striking differences, however, are found in the electronic spectra. Each of these spectra consists of two intense bands at approximately the same wavelength: ~460 and ~600 nm (together with four weaker bands at lower energies). However, the relative intensity of these two bands strongly varies between the four proteins. Plastocyanin has a very strong absorption peak at 600 nm, which is responsible for the intense blue color of this protein. The second, 450-nm band appears as a weak shoulder in plastocyanin. However, this band becomes much more prominent in the (according to their ESR characeristics) rhombic-type proteins pseudoazurin and cucumber basic protein, at the expense of the 600 nm absorption. Nitrite reductase is the limiting case: here the 600-nm absorption peak is reduced by a factor 3 compared with plastocyanin while the 460 nm has become the most intense. As a consequence, nitrite reductase is green rather than blue.

The CASPT2 calculations of the electronic spectra were spectacular *in se*, as they provided the very first fully ab initio interpretation of the spectrum of a chromophore in a metalloprotein. However, on top of that, based on these calculations the relationship between the structural and spectroscopic properties of different blue copper proteins was given a solid explanation. Again, bonding between copper and the cysteine thiolate group was found to play a crucial role. The CASSCF calculations indicated that the thiolate sulphur group has the potential of forming two strongly covalent bonds with the Cu(II) ion, of either $\sigma$ or $\pi$-type. Two different Cu 3d orbitals are involved, and both bonds are constructed by the formation of a bonding–antibonding MO pair with strongly delocalized character over the Cu—S bond. Both bonding MOs are of course doubly occupied in the ground state. However, with nine electrons in the 3d shell, one of the antibonding orbitals is doubly occupied, leaving a single electron in the other antibonding orbital. Both the structure and spectroscopic properties of the copper environment are then determined by the character of the ground state singly occupied orbital (SOMO). In plastocyanin, this orbital has (almost) pure $\pi$ character. It is built from a $\pi$ (anti)bond between two lobes of the Cu 3d orbital in the trigonal plane and the thiolate S $p_\pi$ orbital, the two remaining lobes of the former orbital involved in a $\sigma$-interaction with the nitrogen ligands belonging to the two histidines. As such, no room is left for the methionine, which is present at long distance at the axial position, mainly bound by electrostatic interaction. On the other hand, in the rhombic-type proteins, the ground state SOMO contains a mixture of $\pi$ and $\sigma$ character, the latter gaining more importance as the structure becomes more tetragonally distorted, that is, in the order cucumber basic protein—pseudoazurin—nitrite reductase. As a $\sigma$ bond only takes one lobe of the Cu 4d orbitals, the extra lobe becomes available for $\sigma$ interaction with the methionine, which moves closer to the copper center. The calculations also confirm that the Cu-cysteine bond length increases as the character of this bond moves from $\pi$ to $\sigma$.

Once the differences in ground state electronic structure of these proteins are understood, explanation of their main spectroscopic features becomes straightforward. As confirmed by the CASPT2 calculations, both intense bands in the spectra correspond to charge-transfer states, in which an electron is excited from one of the bonding Cu 3d–cysteine S molecular orbitals, either of $\sigma$ or $\pi$ character, into the ground state SOMO. Excitation out of the $\pi$ orbital takes least energy, and gives rise to the band around 600 nm, whereas the band at 460 nm is due to

excitation out of the $\sigma$ bonding orbital. The relative intensity of these two spectroscopic features is determined by the overlap between both orbitals involved in the transition, hence by the character of the ground state SOMO. In plastocyanin, with its trigonal structure and Cu–cysteine $\pi$ bond, the 600-nm band is strongly dominating, whereas the intensity of this band is decreased in favor of the 460-nm band in the rhomic-type proteins. In a separate study [72], it was shown that also stellacyanin could fit into this picture. Based on its spectral properties, stellacyanin is classified among the rhombic blue copper proteins. However, the copper environmant is in this protein close to trigonal, as it is for the axial proteins. This is shown to be due to the glutamine ligand binding at a much shorter distance to copper than the corresponding methionine ligand in the normal blue copper proteins. This bonding forces a significant amount of $\sigma$-contribution on to the ground state SOMO, such that, even with a trigonal structure the 460-nm band gets a significantly higher intensity than in plastocyanin.

The CASPT2 project on blue copper proteins was performed in a close collaboration between Leuven and Lund in the period 1994–1998. The results were presented in several articles [66, 68–74] and reviews [75, 76], and they marked a milestone in the field of ab initio bioinorganic chemistry, in particular, for the spectroscopic properties. The results of a TDDFT study of the spectra of plastocyanin were presented by Solomon et al. several years later [54] but turned out to fail completely in describing the electronically excited states of this protein, with all ligand field transitions calculated much too high in energy, whereas the charge-transfer states are calculated much too low and in the wrong order.

After the blue copper project was finished, Björn Roos mainly turned his interest toward the chemistry of heavy elements and their description by means of a combined CASPT2-relativistic approach. Only during the last few years, Abhik Ghosh managed to attract his attention again to some problems in bioinorganic chemistry that are troublemakers to DFT [59, 77]. An article that is worthwhile mentioning in this respect concerns the study of the electronic structure of chloroiron corrole by means of CASSCF/CASPT2. In this molecule, the central iron is formally Fe(IV) ($3d^4$) surrounded by a trianionic corrolate ligand and axially coordinated by a $Cl^-$ anion. Making use of CASSCF, it was shown that the actual triplet ground state wave function is rather built from antiferromagnetic coupling between an $S = 3/2$ Fe(III) ion (with configuration $d_{xy}^2 d_{xz}^1 d_{yz}^1 d_{z^2}^1$)

and a corrolate dianion radical, that is, the corrolate ligand is in this complex "noninnnocent." In addition, the CASPT2 results rule out any Fe(IV) state, whether high- or low-spin, within 1.5 eV of the ground state. We believe that the (near) future will indicate this article as a trendsetter in computational studies of metal-heme systems containing metals in (formally) high oxidation states, such as corroles and corrolazines, but also five- or six-coordinated metal porphyrin systems. The latter are very important as possible intermediates in biological reactions involving heme enzymes. The theoretical characterization of the electronic structure of such metal–heme complexes, although already repeatedly reported by DFT [53], still remains a subject of controversy. This is primarily due to the fact that two important aspects involved in the description of the low-lying states in these systems, that is, the variety of possible spin states on the metal and the possibility of noninnocence for the ligands, are in fact both truly problematic for any available density functional today [55, 56, 78–82]. This is already illustrated in two recent CASPT2 studies [60, 83]. The first [60] concerns the electronic structure of compound I, the active intermediate in the cytochrome P450 catalytic cycle, whereas in the second study [83], a CASPT2 investigation of the electronic structure of four-coordinated copper corroles is reported. We are convinced that this is just the beginning of a series of CASPT2 studies in this very intriguing domain of bioionorganic chemistry !

## 6. Personal Perspective

The first time when I met Björn Roos was in 1988, at a conference in Girona, Spain. I was a postdoc at the time, with several years of experience in TM coordination chemistry using mainly semiempirical methods, that is, ligand field theory. I had just set my first steps in ab initio quantum chemistry, already being confronted with the difficulties in treating the open 3d-shell with its many close-lying states, when I found myself sitting in a lecture hall listening to a red-heared man with a loudly carrying voice explaining full of enthusiasm how he had designed a method called CASSCF that was not only capable of handling near degeneracies but could also provide a balanced treatment of all low-lying states in an electronic spectrum. The lecture in fact dealt with electronic spectra of organic molecules, but I clearly remember experiencing at that moment

what is called in German an "Aha-Erlebnis," realizing on the spot that this method was going to be my method of choice in the continuation of my work in computational TM chemistry.

One year later, in 1989, I was one of the participants of the first "Summer School in Quantum Chemistry," organized by Björn Roos in Tjörnarp, Sweden. I have to admit that during this school I became a bit disappointed to have to hear that apparently the largest TM molecules that could be treated with correlated ab initio methods were NiH, NiCO, and so on, and that the primary interest of most of the teachers seemed to be to obtain accurate structures and dipole moments for molecules consisting of two or at most three atoms.

Things of course changed quite rapidly after that. I became involved in the first applications of CASPT2 in TM chemistry. In the beginning of this period of close collaboration between Björn and myself, it still sometimes felt like two different worlds meeting, him with his strong background in physics and physical chemistry, and me coming from of a research group with a tradition in inorganic coordination chemistry. Obviously, we had a lot to learn from each other. At least I know that I have gained so much knowledge from our collaborations that it has had a strong and lasting impact on my scientific career, also at a later stage when our interests had drifted more apart. And I do hope that I have also been able to steer his ideas somehow with my arguments about $\sigma$-donation and $\pi$-backdonation, "nephelauxetic" and "Jahn-Teller" effects, and so on.

One thing is certain: Björn Roos was a very open-minded scientist, who was always looking for actual chemical problems, and was eager to learn the language used to define them. His recent work on the bimetallic systems (section 4) may serve as an illustration. In a way Björn Roos was a lucky man, being able to start his career at the dawn of computational quantum chemistry, develop his "own" computational method, and see this method come to life in so many beautiful applications, by himself and by others. However, to be able to present this kind of pioneering work in so many different domains of chemistry and physics certainly requires a brilliance that is exclusive to just a few among us.

### ACKNOWLEDGMENTS

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