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Theoretical Studies of Electronically Excited States of Molecular Systems Using Multiconfigurational Perturbation Theory

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1. Introduction

In recent years we have seen an impressive development of *ab initio* quantum chemical methods for studies of molecules in their ground electronic state. It is today possible to calculate structures and relative energies for rather large molecules with high precision. The corresponding development for the excited state has been slower. The reason is the larger complexity of excited-state wave functions. The electronic ground state for most systems close to their equilibrium geometry is well described by a single electronic configuration (closed or open shell). An accurate model can use this as the starting point, as is done, for example, in coupled cluster theory. This is not the case for the excited state. Here different electronic configurations are often close in energy and mix heavily. This is also true in the ground electronic state for conformations far from equilibrium, for example, at transition states for chemical reactions, and for weak chemical bonds (the Cr_2 molecule discussed below is an example of the latter situation). A quantum chemical method that aims to be accurate in these situations also has to account for the multiconfigurational nature of the electronic structure.

The computational approach which will be described and illustrated here is based on this concept. The starting point is the molecular orbital, as it is in most modern quantum chemical methods. By occupying the orbitals with electrons, we can form electronic configurations. The orbitals can be singly or doubly occupied. Most molecules in their ground electronic state can be described well by a wave function where the n lowest energy orbitals are occupied by $2n$ electrons. Such a wave function is used in the most common model in quantum chemistry: closed shell Hartree−Fock theory. Excited states are described by electronic configurations with one or more electrons occupying orbitals with higher energies. Different configurations of this type often have similar energies and therefore mix heavily. The wave function is a linear combination of such configurations. Along the reaction path for a chemical reaction, the electronic configuration often changes from one closed shell configuration to another. In the transition-state region, they will again have similar energies, resulting in a wave function which is a linear combination of the two configurations. It is often difficult to decide *a priori* which configurations will be important in a given situation. The multiconfigurational approach avoids this decision by the following method: the orbitals are partitioned into three sets, inactive, active, and secondary orbitals. The secondary orbitals are not occupied in any of the considered electronic configurations. The inactive orbitals are doubly occupied in all configurations. They contain electrons which are well described as closed shells; they do not participate in excitation processes and are not involved in any chemical rearrangement which may take place on the potential surface. The remaining orbitals are active. There are normally less than $2n_a$ electrons which can occupy the n_a active orbitals. Thus, several electronic configurations can be formed. The wave function is constructed as a linear combination of all these configurations with the expansion coefficients and all occupied orbitals (inactive and active) simultaneously optimized such that the energy reaches a stationary value. The method has been called the *complete active space SCF method (CASSCF)* because all configurations are used to expand the wave function, which can be formed by occupying the active orbitals in all possible ways consistent with an overall spin and space symmetry.[1]

The CASSCF method can treat all types of electronic structures, ground states, excited states, radicals, positive and negative ions, etc. It is only limited by the number of orbitals that need to be active, which can be a bottleneck, for example, when many excited states are to be treated simultaneously. CASSCF wave functions will normally give a good qualitative description of the electronic structure. It is, however, not accurate enough for a quantitative assessment of relative energies, such as excitation energies, energy barriers, etc. The reason is that the approach only includes a small fraction of the electron correlation energy. In this respect CASSCF resembles the Hartree−Fock method but with a better treatment of situations where several electronic configurations interact strongly.

Second-order perturbation theory (MP2) has been used successfully for a long time for estimating electron correlation effects in cases where the Hartree−Fock wave function gives a good description of the electronic structure. It was shown 10 years ago that a similar approach could also be used in the multiconfigurational case.[2−4] The starting point is here the CASSCF wave function, which is used as the zeroth-order approximation. The

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first-order correction and second-order energy are computed using Rayleigh−Schrödinger perturbation theory. The method, with the acronym CASPT2, can be used to compute electron correlation effects in all cases where CASSCF is applicable. It has proven to be surprisingly accurate and has found a wide area of application both for ground-state properties and in electronic spectroscopy, where a multiconfigurational approach is needed. The CASPT2 method has been used in a large number of applications, many of them dealing with excited states and electronic spectroscopy. I will give a few illustrative examples below and refer to some recent reviews for more details.[5,6] They have been chosen partly to illustrate the uniqueness of the CASSCF/CASPT2 approach. Several "black box" methods are today available which deal with excited states. One of them is the so-called CI singles approach in the GAUSSIAN program.[7] It is unfortunate that this method is so commonly used, since it gives a very unbalanced description of the excited state and is only able to treat states dominated by singly excited configurations from a closed shell ground state. The same criticism can be made of the recently developed techniques for excited-state calculations based on the density functional approach. The CASSCF/CASPT2 method is, in contrast, completely general and can be used to treat all kinds of electronic states independently of the nature of the ground state and the level of excitation.

2. Potential Curve for the Chromium Dimer

One of the most spectacular applications of the CASSCF/CASPT2 approach concerns the Cr_2 molecule.[8−10] The Cr atom has a ^7S ground state with six unpaired electrons occupying the 3d and 4s orbitals: $(3d)^5(4s)$. Two Cr atoms can therefore, in principle, form six bonds. It is clear that the bonds must be weak since the bond energy is only 1.44 eV (for references to experimental data, see ref 10). As a result, the wave function will be very complex with large contributions from electronic configurations where the antibonding orbitals are occupied. The situation is illustrated in Figure 1, which shows the occupation numbers for the bonding and antibonding molecular orbitals as a function of the Cr−Cr distance. At large distance all occupation numbers are close to 1. This is characteristic of a dissociated bond, where a pair of configurations, one with the bonding and the other with the corresponding antibonding orbital doubly occupied, have equal weight. Moving inward, the 4s bond is first formed, resulting in an increased occupation of the bonding orbital and a corresponding decrease in the occupation of the antibonding orbital. Bonds between the 3d orbitals start to form at a considerably shorter distance.

The same bonding mechanism is found from the shape of the potential curve (cf. Figure 2).[11] We notice that the CASSCF curve is repulsive, except for a weak minimum at a distance of about 3 Å arising from the formation of the 4s−4s bond. A shoulder at about 1.7 Å indicates the possibility of a multiple 3d−3d bond. The CASSCF bond energy is, however, much too low to result in an attractive

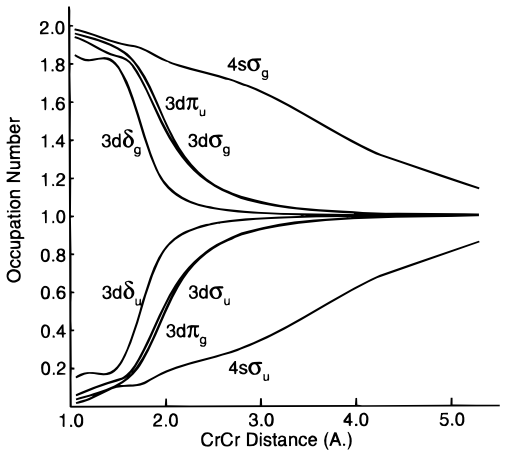

FIGURE 1. Occupation numbers for the bonding and antibonding orbitals in Cr_2 as a function of the CrCr distance (Å). The bonding orbitals have occupation numbers larger than one and are (from top to bottom) $4s\sigma_g$, $3d\sigma_g$, $3d\pi_u$, and $3d\delta_g$. The corresponding antibonding orbitals have occupation numbers smaller than 1. They are $4s\sigma_u$, $3d\sigma_u$, $3d\pi_g$, and $3d\delta_u$.

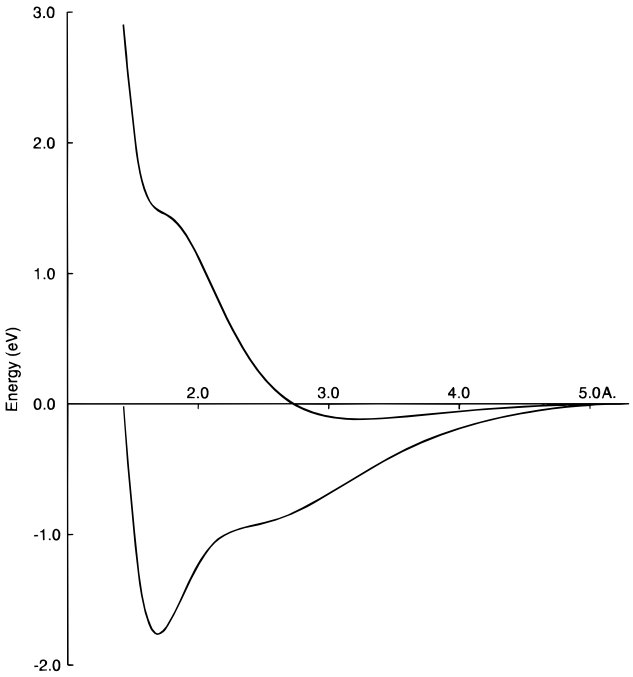

FIGURE 2. CASSCF and CASPT2 potential curves for Cr_2 (energies in eV and intermolecular distance in Å).

potential. The CASSCF wave function is not extensive enough to include a large fraction of the electron correlation energy, which is of utmost importance for Cr_2, where twelve electrons crowd in the same region in space, attempting to form six bonds between the two atoms. This energy is included at the CASPT2 level of theory. The result is a sharp minimum at about 1.7 Å, resulting from the bonding between the 3d electrons. How well developed are these five bonds? Some information about this can be obtained from the occupation numbers. A fully developed single bond has occupation numbers of about (1.98, 0.02) for the pair of bonding and antibonding orbitals. A broken bond has the occupation numbers (1.0,

Table 1. Theoretical (CASPT2) and Experimental Spectroscopic Data for the Ground State of Cr_2

	CASPT2	expt[a]
r_e (Å)	1.695	1.679
ω_e (cm^{-1})	534	481
$\Delta G_{1/2}$ (cm^{-1})	527	452
D_0 (eV)	1.628	1.443 ± 0.056

[a] Experimental data from refs 26−28.

1.0). Inspecting the data for Cr_2 at 1.7 Å, we find the following pairs of occupation numbers: 4s (1.89, 0.11), 3dσ (1.77, 0.23), 3dπ (3.61, 0.39), and 3dδ (3.13, 0.87). A reasonable measure of the bond order may be obtained as the difference between the bonding and antibonding occupations divided by two. This gives 0.89 (4s), 0.77 (3dσ), 1.61 (3dπ), and 1.13 (3dδ). Summing up, this gives a total bond order of 4.40, a quadruple bond. A multiple bond is formed between the two chromium atoms, even if the bond order is considerably smaller than the maximum value 6.

The spectroscopic properties for Cr_2 are presented in Table 1. The experimental data are well reproduced by the CASSCF/CASPT2 method. The agreement is, however, not perfect. This is a reflection of the limitations of the theoretical procedure. Apart from errors due to the use of a limited basis set (the atomic centered functions used to expand the molecular orbitals), it should be remembered that CASPT2 gives only a second-order estimate of the correlation error. It is clear that higher order corrections cannot be neglected. In addition to contributing to the dynamical correlation energy, they will affect the balance between the different contributions to the CASSCF wave function, by decreasing somewhat the weight of the electronic configurations with antibonding orbitals occupied, thus increasing the bonding. The results show, however, that the corrections are small. It should be emphasized that CASSCF/CASPT2 is the only quantum chemical method which today can give a qualitatively and quantitatively correct description of the chemical bond in the Cr_2 molecule.

3. Interacting Double Bonds and the Dark State

Many of the applications of the CASSCF/CASPT2 approach have been in electronic spectroscopy. Electronic spectra for a large number of molecules have been successfully interpreted using this method.[5,6] This is the first time that *ab initio* quantum chemistry has been able to give a consistent and accurate treatment of the electronically excited states over a large number of different types of molecules, including organic systems as well as transition metal compounds. We shall illustrate this here with a discussion of the electronic spectra of conjugated molecules with interacting double bonds. The reason for choosing this example is that it gives a nice illustration of the importance of strong configurational mixing in the valence excited states, because of the appearance of a doubly excited configuration at low energies.

Consider two ethene molecules in a D_{2h} arrangement, but formally noninteracting. The π-system of ethene has two singly excited valence states: the T-state at 4.4 eV and the V-state, where the vertical excitation energy is estimated at 8.0 eV. Combining these states, we can construct the following excited singlet and triplet states for the noninteracting dimer: $^3B_{1u}$ and $^3B_{3g}$ at 4.4 eV (which formally can be written as TN + NT and TN − NT, respectively), $^1B_{lu}$ and $^1B_{3g}$ at 8.0 eV (NV + VN and NV − VN, respectively), and finally the doubly excited states ^3A_g and ^1A_g from the combination TT at 8.7 eV. The interesting observation here is that the doubly excited state occurs at about the same energy as the singly excited singlet state. In a situation where the double bonds are allowed to interact, one can therefore expect to find a doubly excited state at a moderately low energy, or strong mixing between doubly and singly excited states. It should also be noted that transition to the singly excited state NV + VN (the plus state) is strongly dipole allowed, while that to NV − VN (the minus state) is forbidden.

The above description is based on orbitals localized on the two interacting fragments. It is more common to discuss the spectroscopy using orbitals delocalized over the four centers. These are the HOMO − 1, HOMO, LUMO, and LUMO + 1 orbitals used in the discussion below. A transformation between the two pictures is straightforward, but will not be carried out here.

CASSCF/CASPT2 calculations have been performed for a large number of systems involving interacting double bonds.[5,6] These studies include five-membered ring systems,[12,13] linear polyenes,[14−16] norbornadiene,[17] methylenecyclopropene,[18] and cyclohexadiene.[19] We will not discuss all these results here; the reader is referred to the above references for details. It suffices to note that the computed vertical excitation energies are accurate to 0.1−0.2 eV in almost all cases. The results can therefore be used to analyze the importance of the doubly excited state in the description of the low-lying valence excited states. The two lowest excited states can be characterized as the HOMO → LUMO excitation of moderate intensity and the minus combination of the HOMO − 1 → LUMO and HOMO → LUMO + 1 excitations with a variable fraction of the doubly excited configuration $(HOMO)^2 \rightarrow (LUMO)^2$. The intensity of the latter state is determined by the fraction of the doubly excited configuration in the wave function and by the balance between the two components forming the minus combination (a very small intensity results if the two components have equal weight). It is sometimes called the dark state, since it is difficult to observe due to its low intensity. Whether this state is the first or second excited state has been a long-standing issue, which we consider solved now through the series of calculations mentioned above.

As an example, consider the valence excited states of the five-membered rings. The results for four rings, *cis*-butadiene, and benzene are presented in Table 2 and in Figure 3. The electronic spectra of the five-membered rings are characterized by two strong bands superimposed with a large number of Rydberg states (which we will not

Table 2. CASPT2 Excitation Energies (eV) for the Lowest Valence Excited States in *cis*-Butadiene (cB), Cyclopentadiene (CP), Furan, Pyrrole, Thiophene, and Benzene (Oscillator Strengths within Parentheses)[a]

state[a]	cB	CP	furan	pyrrole	thiophene	benzene
$^1A_1^-$ theory	6.04 (0.008)	6.31 (0.0003)	6.16 (0.0015)	5.92 (0.02)	5.33 (0.09)	4.84 (f)
expt		6.2			5.3−5.4 (0.1)	4.90
$^1B_2$ theory	5.58 (0.22)	5.27 (0.15)	6.04 (0.15)	6.00 (0.13)	5.72 (0.07)	6.30 (f)
expt	5.49	5.26	6.04	5.98	5.64	6.20
$^1A_1^+$ theory		7.89 (0.44)	7.74 (0.42)	7.46 (0.33)	6.69 (0.19)	7.03 (0.82)
expt		7.9	7.82	7.54	6.6	6.94
Contributions to the $^1A_1^-$ State from Different Types of Excitations[b]						
HOMO − 1 → LUMO	30	28	30	45	58	
HOMO → LUOM + 1	18	26	23	28	21	
double	50	40	44	25	16	

[a] For detailed references we refer to the individual papers quoted in the text. [b] The summed weights (%) of all configurations of a given type.

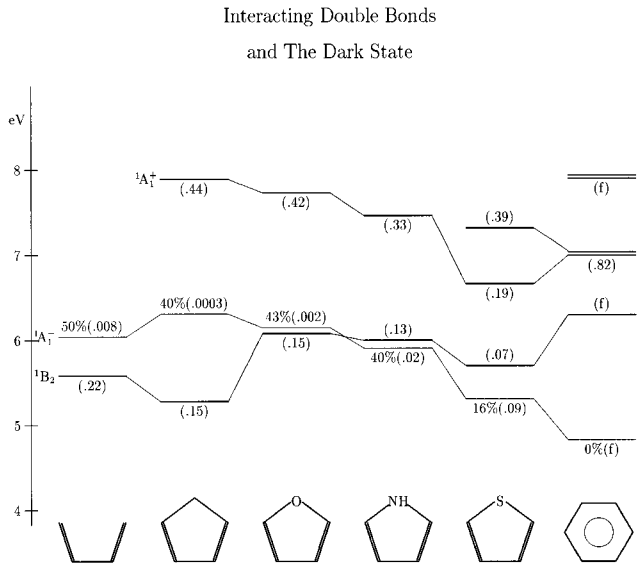

FIGURE 3. Excitation energies for the $^1B_2$, $^1A_1^-$, and $^1A_1^+$ states in a number of molecules with interacting double bonds. The intensities are given within parentheses, and the amount of doubly excited character in the dark state ($^1A_1^-$) is indicated in percent.

discuss here; they have been analyzed in detail in the original publications). The first valence band, of medium intensity, corresponds to the HOMO → LUMO excitation mentioned above with $^1B_2$ symmetry (the molecules have C_{2v} as the common point group). It appears in the energy region around 6 eV. The second and strongest band arises from excitation to the $^1A_1^+$ state characterized as the plus combination of the HOMO − 1 → LUMO and HOMO → LUMO + 1 excitations. It appears in the region between 7 and 8 eV (somewhat lower in thiophene).

Vertical excitation energies and intensities are given in Table 2 together with the experimental energies for the band maxima. The experimental data are well reproduced by the calculations with a maximum error of about 0.1 eV (this is somewhat better than the typical error of the method, which is 0.1−0.2 eV).

What about the dark state, $^1A_1^-$? The calculations show that it has very low intensity (except in thiophene) and that it is hidden under the strong $^1B_2$ band in furan and pyrrole. It is therefore very difficult to locate experimentally, and it has only been found in cyclopentadiene (where it is well separated from the $^1B_2$ band) and in thiophene, where the intensity is higher. The bridging group has an important effect on this state. Interaction with the doubly occupied π-orbital in the bridging group will push up the HOMO − 1 orbital but leave the others unaffected. As a result the HOMO − 1 → LUMO configuration will be stabilized, and its weight in the wave function will increase. At the same time the contribution of the doubly excited configuration will decrease. We can clearly see this effect in going from *cis*-butadiene, where there is no bridging group, to thiophene with the strongly interacting sulfur lone pair. In the first molecule, the doubly excited configuration contributes with a weight of 50% to the CASSCF wave function, which decreases to 16% in thiophene.The contribution of the HOMO − 1 → LUMO configuration increases from about 30% to almost 60%.

The coupling via the bridging group also affects the energy and intensity. The increase in intensity arises from the changed balance between the HOMO − 1 → LUMO and HOMO → LUMO + 1 configurations and the decreased weight of the doubly excited configuration. This effect is apparent in pyrrole and even more in thiophene, where the intensity of the $^1A_1^-$ state is close to 0.1 (the computed and experimental values agree). At the same time as the intensity increases, the energy decreases. Since the $^1B_2$ state is not affected in the same regular way, the relative energy of the two states will change, and in pyrrole and thiophene the $^1A_1^-$ state becomes the lowest excited singlet state.

A similar situation obtains in the linear polyenes where the crossover between the HOMO → LUMO state and the dark state occurs for a chain length of eight carbon atoms (octatetraene).[14−16] Norbornadiene is an example of a system where the coupling between the double bonds is weak. Here the dark state appears as a purely diexcited state (forbidden by symmetry) at an energy of 7.49 eV.[17] As a final example, let us mention 1,3-cyclohexadiene, where the hyperconjugative coupling between the double bonds places the HOMO → LUMO state at a low energy (4.72 eV) while the dark state is found at 6.18 eV with an intensity of 0.004.[19] Finally, I emphasize again that of the different approaches used today in quantum chemistry to treat excited states, it is only the CASSCF/CASPT2 approach (or related multiconfigurational based methods) that gives a proper description of the dark states in conjugated molecules.

4. Blue Proteins

As a final example of the applications of the CASSCF/CASPT2 method in electronic spectroscopy, we shall consider a biochemical system: the so-called blue proteins. This class of copper proteins (the cupredoxins) have been studied extensively for many years due to their peculiar physical properties (again, I will not give specific references, but the interested reader is referred to a recent review article, where all appropriate references may be found[20]). They have unusually high reduction potentials and EPR spectra with narrow hyperfine splittings and a varying degree of rhombicity. What will interest us especially here is their intense color, usually blue, which is due to a charge transfer (CT) excitation from the sulfur lone pair on a cysteine ligand to the 3d hole on the Cu(II) ion.

Such CT excitations usually occur at rather high energies, well above the normal d−d transitions. The cupredoxins are, however, different. Here the first CT bands occur close to the ligand field transitions at about 1−12 eV. The reason is the uncommon coordination sphere of the copper ion. Unlike most inorganic copper complexes, the Cu ion in most of these proteins is four-coordinated with a very plastic structure, which can shift from trigonal to distorted tetragonal depending on the detailed structure of the surrounding protein. Important for the properties is also the presence in all of these proteins of a cysteine ligand with the sulfur ion tightly bound to the copper.

There is a close relation between the structure of the coordination sphere around copper and the spectroscopic properties of the protein. Most of the cupredoxins have four ligands attached to the copper ion: cysteine (Cys), two histidines (His), and a methionine (Met). Large variations are found in the Cu−S distance to the weakly bound Met ligand, while the other distances vary much less. The geometrical arrangement is intermediate between the tetragonal coordination normally preferred by Cu(II) and the tetrahedral geometry of Cu(I) (the geometry of the blue protein plastocyanin is shown in Figure 4). The cupredoxins serve as charge-transfer proteins, and the similarity between the geometries of the oxidized and reduced forms results in a small reorganization energy, which allows for a high rate of electron transfer.

Historically, it has been assumed that the unusual geometry of the active site in the cupredoxins is a result of protein strain, which would force the ligands into a distorted trigonal structure instead of the tetragonal structure normally preferred by the Cu(II) ion with four ligands. Theoretical calculations have, however, shown that the trigonal structure preferred in the oxidized form of the blue protein plastocyanin (an example of the so-called axial type 1 copper proteins) is a result of the chemical bonding between the Cu(II) ion and the Cys ligand. The lowest energy is obtained for an electronic configuration where the bond involves the π lone pair of the sulfur atom interacting with the half-filled $3d_{xy}$ orbital of the metal.[21] The resulting structure will have a short

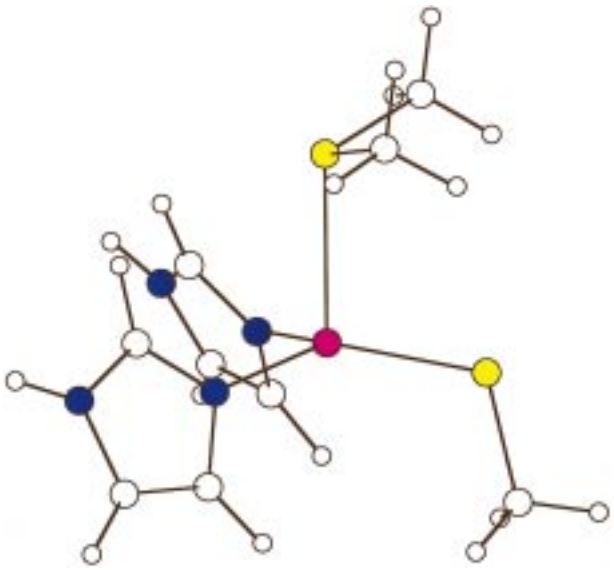

FIGURE 4. Geometry of the active site in the blue protein plastocyanin. The ligands are modeled as SCH_3 for Cys, imidazole for His, and $S(CH_3)_2$ for Met. The color code for the atoms are Cu, red; N, blue, S, yellow; and C, H, white.

$Cu-S_{Cys}$ distance (2.11 Å), two short $Cu-N_{His}$ bonds (1.03 Å), and a long $Cu-S_{Met}$ bond (2.71 Å), in good agreement with the experimental structure for plastocyanine. No strain is thus needed to obtain this configuration. The potential surface is, however, extremely flat. Only a few kilojoules per mole is needed to change the structure to distorted tetragonal where the bond between Cu and Cys is instead of σ-type (cf. Figure 5). This is the situation in the so-called rhombic type 1 copper proteins, for example, nitrite reductase. The detailed structure of the active site is determined by the surrounding protein and can vary considerably for different types of proteins. We will not go further into the details of the structural properties of the cupredoxins here; the reader is referred to the recent review for more details.[20] Instead we shall see how the spectroscopic properties may be modeled using the CASSCF/CASPT2 approach, and how they are related to the structure.

A signature of the cupredoxins is their color, blue for plastocyanin, green for nitrite reductase, and even yellow for some mutated azurins, where methionine has been replaced by a more strongly bound ligand. Electronic spectra have been computed for a number of models of the active site in these proteins using the CASSCF/CASPT2 approach.[20,22,23] To compute the electronic spectrum of a protein is not a trivial task. The active site, where the light is adsorbed, must be modeled by some simpler system. The effect of the remaining part of the protein and the solvent has to be included in some approximate way. The structure of the active site is another problem. Experimental structures have considerable uncertainties, and it is better to use geometries determined theoretically. Ideally, electronic spectra should be computed with the geometry optimized at the same level of approximation as is used for the spectrum. Such an approach is, however, not practically feasible for a system as compli-

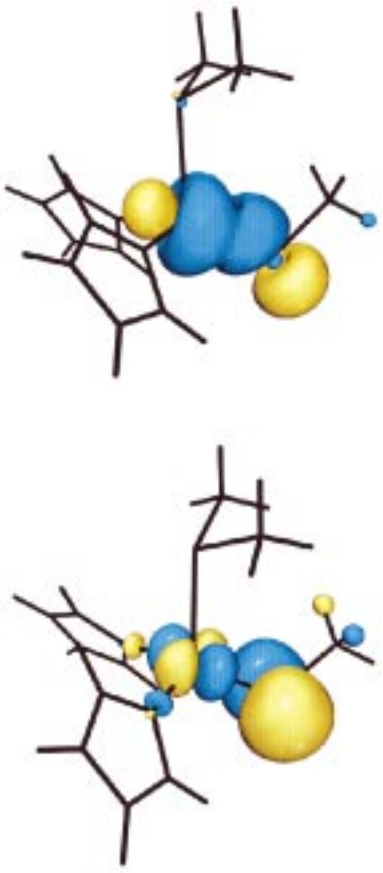

FIGURE 5. Half-filled orbital in the π-bonded (lower) and σ-bonded (upper) $Cu(His)_2(Met)(Cys)^+$ complexes, respectively. The former is the ground state in plastocyanin and the latter in nitrite reductase. The complex is modeled as $Cu(imidazole)_2(S(CH_3)_2)(SCH_3)^+$.

cated as a protein. Instead the geometry is optimized at a lower level of theory (density functional theory was used with the crucial Cu−S distances optimized separately using the CASPT2 method).

The CASSCF/CASPT2 method has been used successfully for the calculation of electronic spectra for a large number of first-row transition metal compounds.[6] This type of application is, however, far from trivial, since the demands on the active orbital space are large (sometimes too large to make the calculations possible). The reason is the strong electron correlation in the 3d shell for transition metals to the right in the periodic table, which cannot be completely accounted for at the CASPT2 level. The most crucial radial correlation has to be determined at a higher level of approximation (CASSCF). Therefore, the active space has to include two sets of 3d orbitals (the normal occupied orbitals plus one set of correlating orbitals). Thus, 10 orbitals are needed already for the metal atom (of course, not all these orbitals are pure metal; some of them may be involved in the ligand bonding and therefore more or less delocalized). This leaves only a few to describe the ligand orbitals not involved in the metal−ligand bonds, since the limit of the method is 12−14 active orbitals. An example of a difficult case is MnO_4^-, which needs 17 active orbitals (5 3d plus 12 2p derived ligand orbitals).[24] The low-energy bands of the cupredoxins involve ligand field excitation and charge transfer from the Cys sulfur lone pair orbitals. An active orbital space of 12 orbitals (with 13 active electrons) is therefore sufficient to describe their spectra.

We shall illustrate the electronic spectra for these compounds by discussing briefly the results obtained for the oxidized forms of plastocyanin and nitrite reductase. These two proteins have different ground states and as a result also different geometries, even though the ligands around the copper ion are the same. Plastocyanin has a trigonal structure resulting from a π-bonded Cys ligand (cf. Figure 5), while the structure of nitrite reductase is distorted tetragonal with the Cys ligand σ-bonded. The geometrical parameter most sensitive to the change in structure is the angle between the $N_{His}-Cu-N_{His}$ and the $S_{Met}-Cu-S_{Cys}$ planes. This angle is 90° for the trigonal structure, while it would be 0° or 180° for a planar tetragonal structure. The value in plastocyanin is 90°, while it is 62° in nitrite reductase (theoretical results). As a consequence the $Cu-S_{Met}$ distance will be longer in plastocyanin, 2.67 Å compared to 2.42 Å in nitrite reductase. These structural differences will have a profound influence on the spectroscopic properties.

$Cu(imidazole)_2S(CH_3)_2SCH_3^+$ has been used as a model for the active site, and the electronic spectrum has been computed using the methods described above.[25] The effect of the surrounding protein was included in a point charge model. The results are shown in Table 3. The electronic spectrum for the trigonal model is shown to the left in the table. The ground state for this structure has the (Cu−S)π^* orbital singly occupied. All excitations move one electron into this orbital to make it doubly occupied. The lowest excited state corresponds to an excitation from the (Cu−S)σ^* orbital and occurs at low energy, which illustrates the closeness of the two possible ground-state electronic configurations. The next three electronic states correspond to ligand field (LF) excitations. The most intense transition is from the bonding (Cu−S)π orbital. This is formally a charge-transfer (CT) excitation,

Table 3. Comparison between the Calculated and Experimental Spectra of Plastocyanin and Nitrite Reductase (Energies in eV)

	plastocyanin		nitrite reductase		
	calcd	expt	calcd	expt	
(Cu−S)$\sigma^* \rightarrow$ (Cu−S)π^*	0.54 (0.000)	0.62 (0.000)	0.55 (0.000)	0.69 (0.000)	(Cu−S)$\pi^* \rightarrow$ (Cu−S)σ^*
$Cu3d_{z^2} \rightarrow$ (Cu−S)π^* LF	1.44 (0.000)	1.34 (0.003)	1.53 (0.000)	1.48 (0.003)	$Cu3d_{z^2} \rightarrow$ (Cu−S)σ^* LF
$Cu3d_{yz} \rightarrow$ (Cu−S)π^* LF	1.61 (0.003)	1.59 (0.011)	1.60 (0.000)	1.67 (0.009)	$Cu3d_{yz} \rightarrow$ (Cu−S)σ^* LF
$Cu3d_{xz} \rightarrow$ (Cu−S)π^* LF	1.57 (0.000)	1.73 (0.004)	1.72 (0.003)	1.85 (0.010)	$Cu3d_{xx} \rightarrow$ (Cu−S)σ^* LF
(Cu−S)$\pi \rightarrow$ (Cu−S)π^* CT	1.94 (0.116)	2.07 (0.050)	1.96 (0.032)	2.18 (0.020)	(Cu−S)$\pi \rightarrow$ (Cu−S)σ^* CT
(Cu−S)$\sigma \rightarrow$ (Cu−S)π^* CT	2.72 (0.001)	2.65 (0.004)	2.78 (0.119)	2.72 (0.030)	(Cu−S)$\sigma \rightarrow$ (Cu−S)σ^* CT

but the charge flow is small since the two orbitals involved are both delocalized over the Cu and S atoms as a bonding−antibonding pair. As a result, the intensity is large, and it is this excitation that gives rise to the blue color in plastocyanin and other trigonal cupredoxins. The CT transition from the (Cu−S)σ bonding orbital appears at a higher energy, but with a very low intensity.

To the right in Table 3 we find the spectrum for the tetragonal structure where the (Cu−S)σ* orbital is singly occupied in the ground state. All excitations are now into this orbital. The two spectra are very similar with one important exception. The relative intensity of the two CT transitions has changed such that the upper is now more intense. This feature of the spectrum is nicely reproduced by the calculations, even if the relative intensity in both cases is somewhat too large. It is this change in intensity that explains the green color of nitrite reductase.

Calculations have also been performed for other cupredoxins like cucumber blue and stellacyanin,[20,23] and they confirm the close relation between the structure and the spectral properties. The example shows that advanced *ab initio* quantum chemistry can now be used to tackle spectroscopic problems also in biochemical systems.

5. Conclusions

I have tried to illustrate with three examples how the multiconfigurational approach in quantum chemistry can be used to model complex electron structure problems in chemical binding and electronic spectroscopy. The first example illustrates the complexity of the chemical bond in the chromium dimer with its six weak bonds. Today there exists no alternative to a multiconfigurational based method for the theoretical explanation of the binding in this and similar systems.

As a second example, I have chosen the valence excited states in organic molecules with interacting double bonds. It was shown that a state with considerable doubly excited character appears among the low-lying excited states, sometimes even as the lowest state. There is no alternative to a multiconfigurational approach which can handle such a situation adequately.

Finally, the blue proteins were used to illustrate how the present approach can be used in transition metal chemistry. Here, the difficulties are larger, and there are many cases which cannot today be treated with the CASSCF/CASPT2 method, primarily because the demands on the active space are too large. This is a technical problem which may be solved in the future. The alternative today is to use the coupled cluster approach, which has recently shown some promising results for singly excited states. This is, however, a much more expensive approach and may also be difficult to apply generally in transition metal chemistry with its often degenerate and open shell ground-state electronic structure.

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