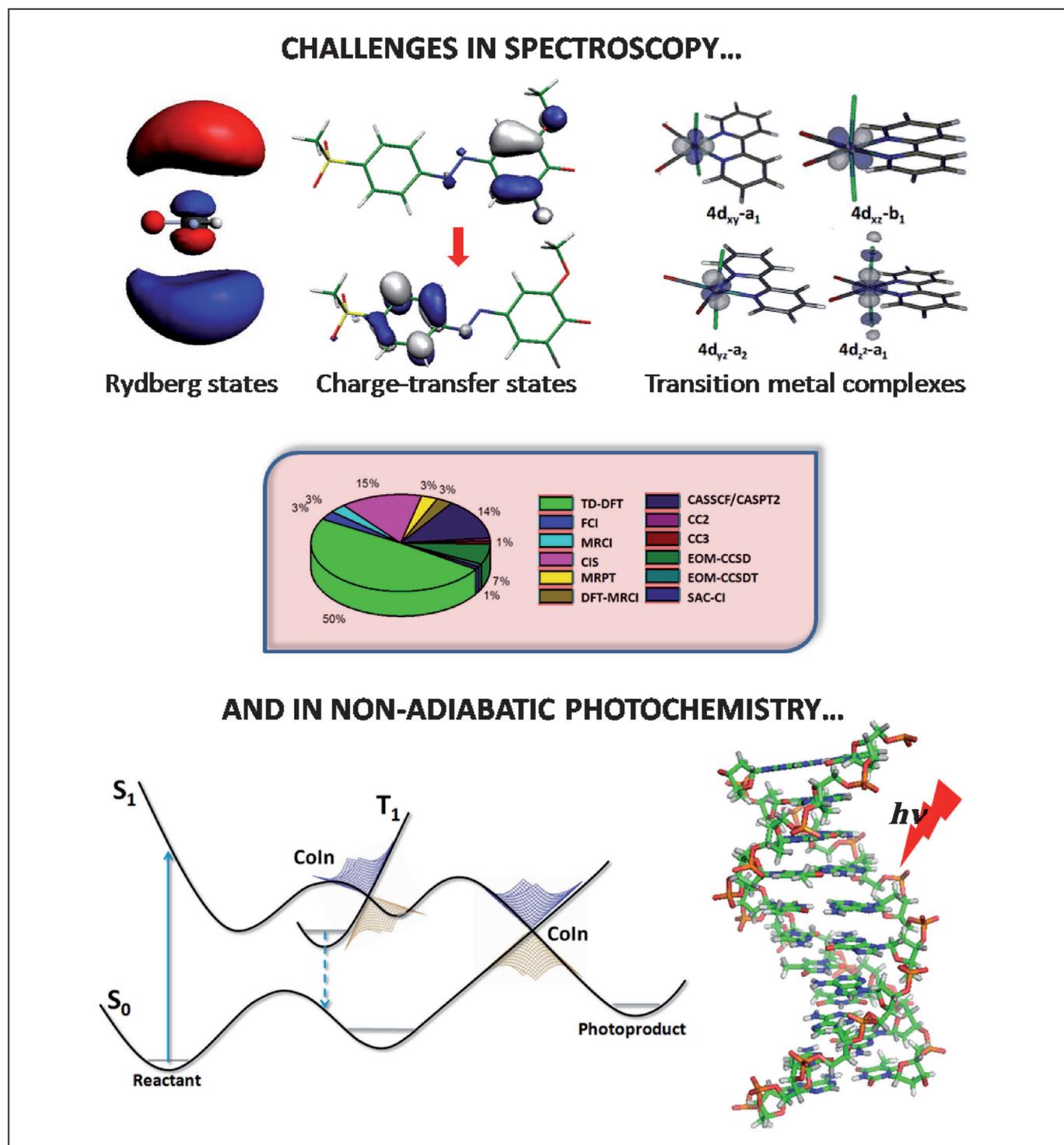


Progress and Challenges in the Calculation of Electronic Excited States

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A detailed understanding of the properties of electronic excited states and the reaction mechanisms that molecules undergo after light irradiation is a fundamental ingredient for following light-driven natural processes and for designing novel photonic materials. The aim of this review is to present an overview of the *ab initio* quantum chemical and time-dependent density functional theory methods that can be used to model spectroscopy and photochemistry in molecular systems. The applicability and limitations of the different methods as well as the main frontiers are discussed. To illustrate the progress achieved by excited-state chemistry in the recent years as well as

the main challenges facing computational chemistry, three main applications that reflect the authors' experience are addressed: the UV/Vis spectroscopy of organic molecules, the assignment of absorption and emission bands of organometallic complexes, and finally, the obtainment of non-adiabatic photo-induced pathways mediated by conical intersections. In the latter case, special emphasis is put on the photochemistry of DNA. These applications show that the description of electronically excited states is a rewarding but challenging area of research.

1. Introduction

An electronic excited state is obtained when a molecule is in an energy level higher than the ground state, for example, after absorption of one or more quanta of light (photons). While the ground state of most molecules at the equilibrium geometry is reasonably well described by a single electronic configuration, this is not the case for excited states. For this reason, while the description of chemical structures in the ground state can be considered close to routine, those of the excited state structures is still a great challenge. Understanding ground-state reactivity is demanding and certainly can be complicated. However, anyone dealing with excited states knows that photochemical calculations are usually intricate, time-consuming, and in some cases very involved. These are due to the oft multiconfigurational character of the electronic structure of excited states, the need to describe short- and long-range interactions, the presence of metals, the large amount of degrees of freedom that relaxation involves, and last but not least, the size of the systems of interest. However, and despite some frustrations, there is a fascination in computing excited states and understanding photochemical reactions. The possibilities that a molecule has after electronic excitation are plenty and the disentangling of these mechanisms has thrilled computational chemists for several decades.

The XXIst century might be very well the century of light. Understanding and controlling photoexcited systems will be crucial for future research in many branches of optics and photonics. The sun is one of the main sources of photons that can be converted into many functions and applications. The discovery of lasers more than 50 years ago represents one of the most important revolutions in modern science. Since then, the laser has rapidly advanced the field of information technology. However, many of the processes which have yet to be optimized invariably rely on understanding how light interacts with matter. Therefore, for a chemist it has become indispensable to comprehend in detail the interaction between light and molecules.

A number of experimental techniques, and in particular time-resolved spectroscopy, are available today to probe the electronic and structural properties that molecules undergo after light excitation.^[1,2] Electronically excited molecules differ from the ground state in the distribution of electrons, giving

rise to important structural changes. The study of these new properties of photoactive molecules is of fundamental importance in many different fields of science. Time-resolved absorption and emission spectroscopy, for instance, can give information on the electronic properties of transient states and provide kinetic profiles of formation and decay generated along a photophysical pathway. However, interpretation of the recorded spectra as well as unveiling the molecular stages experienced by the photoactive molecule requires a strong synergy between spectroscopists and theoreticians. Indeed, most of the time the interpretation of absorption and emissive properties, transients, and excited-state dynamics is difficult to handle without the valuable help of quantum chemical and dynamical calculations. The calculations can provide a detailed assignment of absorption and emission spectra, as well as of the electronic geometries that a molecule visits along its relaxation path, with quantum yields and time scales.

The rich spectral and photochemical experimental data is a subtle interplay of several effects of different nature. Among them, vibronic contributions and solvent effects are important ingredients. The treatment of solvent effects in computational chemistry (also for the ground state) can be done in different ways. The explicit consideration of one or more solvation shells can become prohibitive quickly for excited states. Instead, cavity models are preferred. In those, only bulk effects are taken into account. The polarizable continuum method (PCM)^[3,4] or the conductor-like screening method (COSMO)^[5] are easily implemented in standard packages and combined with many kinds of quantum mechanical (QM) methods. The

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PCM (or COSMO) procedure is usually sufficient to account for the solvent effect on the spectroscopic parameters, except when dealing with protic solvents which can establish explicit hydrogen bonds. In these cases it has been shown that a first shell of explicit solvent molecules in combination with the bulk effects at the PCM level are mandatory to get spectroscopic accuracy.^[6,7] Hybrid techniques, such as quantum mechanical/molecular mechanics (QM/MM) are the most convenient approach to mimic environmental solvation, or as it will be pointed out in some applications below, the effects of biological surroundings. For a detailed description of solvent and vibronic effects on spectroscopic properties we refer the reader to excellent reviews in the field, for example, refs. [8] and [9] and references therein. Spin-orbit effects also play an important role in the deactivation of photoactive molecules and, especially when heavy transition metals are involved, in photoluminescence properties, due to transitions between singlet and triplet states. The understanding and manipulation of the spin in materials and organic semiconductors has important consequences for future device applications.

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The objective of this review is to provide an overview of the methods currently available to treat electronic excited states and to show where we are now and how much we have achieved. We discuss the main features of the most widely used methods, their applicability, and most importantly, their flaws and limitations. Although the field of excited states has advanced tremendously since its beginnings several decades ago, there is still plenty of room for improvement. Three playgrounds are selected to illustrate the progress of this field. Needless to say, the choice of those is a licence of the authors, likely driven by our own interests and experience. These fields are: 1) Computational spectroscopy focusing on organic chemistry, which is one of the fundamental applications of excited states and as such, it was the first target of the early calculations on excited states. We found it relevant to discuss which obstacles are still facing the current methodologies, as well as how many mountains have nonetheless been eroded. 2) The calculation of excited states in systems containing metals, a field that is more difficult to deal with than excited-state organic chemistry. Here we have reviewed problems specific to metals, as well as discussed strategies that are currently used and that can be exploited in the future. 3) Finally, we concentrate on photochemistry because it is the very last step which is required to design (and control) novel photonic materials with applications across many fields of science. Computational photochemistry is the culmination of excited-state chemistry. In order to illustrate how very often a detailed understanding of the fate of photoexcited molecules requires the synergy of quantum chemistry, dynamics and experiment, we have chosen DNA. The main achievements, challenges, and frontiers in this field are discussed and put in perspective.

Although the field of excited-state chemistry is young, the number of publications dealing with excited states has exploded over the past years. We apologize for not being able to cite all of the valuable papers. The rest of this review is organized as follows: In Section 2, the computational methods are described. For simplicity they are divided into single-configurational-, multi-configurational-, and density functional theory (DFT-) based. In Section 3, the three different applications are presented. An outlook is given in Section 4.

2. Computational Methods for Excited States

Quantum chemistry usually relies on the calculation of the lowest-energy solution of the electronic Hamiltonian operator, representing the ground state of the molecule. On the other hand, electronic excited states are obtained as higher roots of the operator, a procedure that requires much more complex resolution algorithms. Ground-state representations are essentially based on the Hartree-Fock (HF) single-configurational description of the wave function, which provides a reference wave function for the electronic ground state and a set of molecular one-electron spin-orbitals, both occupied and unoccupied, representing the ground-state configuration.^[10,11]

2.1. Single-Configurational Ab Initio Methods

Configuration Interaction Methods

The description of an excited state can be described at least qualitatively with the configuration interaction-singles (CIS) approach. The CIS method is based on an expansion (with a reference HF wavefunction) limited to all possible single excitations either in terms of determinants or configuration state functions (CSFs, symmetry-adapted linear combination of Slater determinants). The singly-excited states are orthogonal to the ground state because of the Brillouin theorem, but not necessarily to each other. The orthogonalization of the states is the essence of the CIS technique, which involves diagonalization of the configuration interaction matrix formed from the HF reference and all single excited configurations. The final outcome is a set of energy eigenvalues associated with eigenvectors in which the coefficients of the singly excited determinants, variationally obtained, characterize the state.

The most appealing feature of CIS is that it is relatively fast compared to other methods and therefore it can be applied to large systems.^[12] It delivers reasonable energies for cases where the ground state and the excited state are well-described by a single configuration. Charge transfer transitions often fall into this category, and then the simple CIS approach can be appropriate, although it tends to grossly overestimate the vertical excitation energies.^[13,37] However, the number of systems which require more than one configuration is not small. For instance, systems where purely doubly-excited states exist at low energies cannot be described with CIS.^[14] The well-known 2^1A_g state of polyenes, one of the main protagonists in photochemistry, is a good example. In planar 1,3-butadienes

no A_g states can be obtained at the CIS level of theory. Another deficiency of the CIS method is that it does not include the most basic correlation effects and therefore errors larger than 1.5 eV are quite common. Electronic states are often incorrectly ordered^[10] because the differential correlation energy affects the excited states unevenly. This is more dramatic when the intrinsic character of the states is multiconfigurational. Attempts to improve CIS by using double excitations or perturbation theory have not been very successful.^[15] Improved results have been obtained with semiempirical parametrizations of the CIS matrix elements, for instance using the INDO/S approach.^[10] Nevertheless, in summary, the CIS method is clearly unsafe and its use is discouraged because the results obtained are usually misleading.^[16,17]

Propagator Approaches

Although less popular in the last years, an alternative to computing excited state is to use propagator approaches.^[18] The underlying technique, also called the Green's function approach, equation-of-motion or linear response theory in its different forms, can be applied to various types of methodologies, whether single- or multi-configuration interaction, coupled-cluster, or density functional. The basis of the technique considers that once a molecule is subjected to a linear time-dependent electric field fluctuating with a certain frequency, a second-order property such as the frequency-dependent ground-state polarizability of the system is well approximated by the relation between the square of the transition dipole moment in the numerator and the difference in state energies in the denominator.^[19] Using complex function analysis, it is possible to obtain the poles of the expression, that is, the values for which the frequency corresponds to the excitation energies and the denominator goes to zero, whereas the residues provide the numerators, in this case the one-photon absorption matrix elements. Higher-order quadratic response theory determines third-order molecular properties, as the first hyperpolarizabilities, and from them two-photon absorption matrix elements. The peculiarity of the propagator approaches is that the wave functions of the individual states are not necessarily computed to obtain excitation energies and transition probabilities, while its quality relies on the type of reference wave function.^[19]

A hierarchy of approximate propagator methods can be defined as a function of the selection of the order of the particle-hole replacement operators. The random-phase approximation (RPA) or time-dependent Hartree-Fock (TDHF) approach uses the HF ground state as reference and employs a single replacement operator.^[19] Further developments of the method have included second-order perturbation (MP2-) based approaches such as the second-order polarization propagator approach (SOPPA) method, in which density-shift terms, particle-particle and hole-hole, are included.^[20] The second- and third-order algebraic-diagrammatic construction (ADC) approach, a Green's function one-electron propagator technique, has been applied in recent years to different cases.^[21] Methods based on Green's function belong to the

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same hierarchy of approaches, although they are typically expressed in the energy-dependent formalism, which can be transformed to the time-dependent propagator formalism by using a Fourier transform. One-particle many-body Green's functions methods are basically employed to compute ionization potentials and electron affinities.^[10]

Usual errors of the RPA method fall into ± 1 – 2 eV in the excitation energies, while oscillator strengths may differ in one order of magnitude. The effect of double excitations has been included by perturbation theory in order to slightly improve the excitation energies in the RPA(D) approach.^[22] The SOPPA approach may improve the results within ± 0.6 eV. Similar behavior is displayed by the ADC(2) method, slightly improved in the third-order version.^[23] In any case, all these methods do not include non-dynamic correlation effects and, because of their single-configuration character, are extremely deficient when computing multiconfigurational states, or doubly excited states. The improved versions of the methods, SOPPA and ADC(3), can be used to obtain a good qualitative description of the spectrum, although they lack generality. Compared to other methods they have, supposedly, the desired black-box behavior, and with respect to the TD-DFT approaches, their failures are not erratic, but well-justified. On the other hand, multiconfigurational methods (see below) in combination with response theory (either linear-response or quadratic response methods) have been recently developed.^[24] As a general remark, they have shown to be accurate in the calculation of molecular properties, but not so much in energies.^[24]

Coupled-Cluster Methods

The most accurate family of methods for excited states based on a single configuration that have known a practical use, at least for small- and medium-size systems, are those based on the size-extensive coupled-cluster (CC) approach. The key point of single-configuration CC approaches for excited states is that even if they still use a HF zeroth-order reference, which is in general rather poor for representing excited states, the large amount of correlation is included with high orders in the excitation level. The poorer the representation of the ground-state reference, the higher the required level of excitation, sometimes up to an unaffordable point.

The CC methods employed most often have been the symmetry-adapted cluster configuration interaction (SAC-CI) approach,^[25] the equation-of-motion coupled-cluster (EOM-CC) method (also the similarity-transformed STEOM-CC^[26,27]), and the hierarchy of linear-response CC x approaches.^[28] Although they have different formulations, their results for the common truncated and non-approximated coupled-cluster models are similar. The SAC-CI method, which has been used to compute large systems by approximate procedures, and has been also extended to open-shell references, is comparable to the EOM-CCSD approach, which includes up to double-excited cluster operators.^[29] The family of CCS, CC2, CCSD, CC3, and CCSDT methods are based on response theory. Poles and residues of the linear-response CC equations yield excitation energies and transition matrix elements. CCS, CCSD, and CCSDT give a com-

plete coupled cluster treatment of single, single-double, and single-double-triple spaces, respectively, for excited states. The CCS approach is equivalent to the single excited configuration interaction or Tamm–Dancoff approach.^[30] The iterative hybrid CC2 and CC3 procedures introduce approximations of similar nature, although differing in the level of excitation. In this way, in CC2 the doubles of the CCSD approach and in CC3 the triples of the CCSDT approach are approximated by using perturbation theory up to the first- and second-order, respectively.^[28,31] CC3 includes the single and double excitations at the third order and the triple excitations at second order in the fluctuation potential, all of them one order higher than CCSD.^[11]

In order to get accurate excitation energies and properties, the single-configuration CC methods should include high excitation levels to compensate for both the poor reference wave function and the multiconfigurational character of the excited states. In situations where the HF reference is good enough, CC-based methods are, up-to-date and in practice, the most accurate methods to compute excited states in small to medium-size molecules with closed-shell ground states, but only for those states which are described well by single excitations and in systems where the ground state is clearly monon-configurational. Weaknesses are related to low levels of excitations employed in situations where the single-configuration reference is clearly poor, for instance dissociating or quasi-degenerated situations or systems like ozone, C₂, N₂, the NO dimer and others.^[10,11,32–34] In those cases, triple or higher excitations have to be included in the cluster expansion. In a recent benchmark study on excitation energies^[35] it was shown that CCSD or CC2 is less accurate than complete active space perturbation theory of the second order (or CASPT2, see below)—in the ionization-potential–electron-affinity (IPEA) formulation^[36]—for systems with closed-shell ground states. However, it is fair noting that the specific energy differences in IPEA are parameterized from experimental values, and therefore it is not surprising that is more accurate when applied to systems and for properties that have been included in the training set. CC methods lose precision when the character of the states is clearly multiconfigurational. For instance, the 2¹A_g state of polyenes is again a good example. CC2 and CC3 in hexatriene deviate^[38] by 1.43 and 0.52, respectively, from the experimental two-photon value (5.21 eV).^[39] Similar errors are found in other polyenes, also using EOM-CC techniques.^[40] In contrast, the CASPT2 vertical result of 5.20 eV^[41] can be considered an excellent benchmark. Another example is the 1¹E_{1g} state of ferrocene, with an error of 1.5 eV from experiment at the CC2 level.^[42] In cases where even the ground state is clearly multiconfigurational, such as the ozone molecule, the errors are even more dramatic. For instance, the CC description of the states of ozone leads to a 2.3 eV error for the 1¹B₂ state at the CCSD(T) level and 4.5 eV error for the 2¹A₁ state at the EOM-CCSD level.^[34] A similar situation occurs for some excited states of C₂, showing deviations with respect to full CI (FCI) of 2.05, 0.86, and 0.41 eV at the EOM-CCSD, CC3, and EOM-CCSDT levels.^[34] Other pathological case is the description of the electronic states of the NO dimer, N₂O₂, where EOM-CCSD fails at

describing even the ground state, and EOM-CCSDT shows large inaccuracies in describing the excited states.^[33]

Large improvements in the CC description of multiconfigurational and degenerate situations have been reached with the completely renormalized coupled-cluster (CR-CC) approach, whose use needs to be generalized.^[43] Multireference coupled-cluster (MRCC) methods have been a long-time promise of accuracy and generality that has not been completely fulfilled, although there have been many attempts to develop efficient algorithms.^[44]

2.2. Multiconfigurational *ab Initio* Methods

In very many cases the use of a single configuration is inadequate. The typical case is the molecular bond-breaking process, in which at least two configurations are needed along the reaction coordinate to properly describe the dissociation process: the closed-shell bonding and the open-shell antibonding situations. Many other cases hold, like excited states, biradicals or conical intersections (CoIns). In these cases a new CI-type wave function can be expanded into a many-electron basis set of spin-adapted CSFs or determinants. In cases where the reference wavefunction is not the single HF Slater determinant but a suitably defined set of determinants, the process is denoted as multi-reference CI (MRCI). In the case where the energy is obtained by minimizing both the optimum CI expansion coefficients and the optimum form of the orbitals the approach is known as the multiconfigurational self-consistent field (MCSCF) method. The characteristic advantage of the MCSCF-based approaches against all other electronic structure methods is that, provided a proper reference CI wave function is obtained, they are totally general and they can deal with any electronic structure problem, unlike single-reference methods.

Designing a MCSCF calculation, however, is tough work. One different solution is obtained from each of the multiconfigurational wave functions, which should be selected in the way that, first, allows the proper description of the studied process in all regions of the potential energy hypersurface (PEH), and, second, the final solution (obtained after inclusion of the remaining correlation effects) is obtained as the result of a balanced selection of the reference CIs. Techniques were used to make this selection feasible by using, for instance, perturbation theory to estimate the weight of the different CIs to the reference wave function^[45,46] or orbital occupation numbers.^[47] A more balanced choice is, however, obtained by selecting the specific orbitals and electrons entering into the chemical process with chemical criteria. This is the cornerstone of the complete active space (CAS) SCF approach developed by Roos and coworkers in 1979.^[48,49] In the CASSCF method, the orbitals are classified in three categories, depending on the role they play in building the many-electron wave function: inactive, active, and secondary orbitals. Inactive and active orbitals are occupied in the wave function, whereas the remaining of the orbital space, given by the size of the one-electron basis set employed, is constituted by secondary orbitals, also called external or virtual. Inactive orbitals are doubly occupied in all the

CASSCF configurations, and are also optimized in the variational process but treated as in the restricted HF function. The rest of the electrons are placed in the active orbital space and should be those responsible of the description of the chemical process.

The CASSCF wavefunction is a full CI wavefunction constructed with the set of active orbital and electrons that is named CAS CI. Also, if the CASSCF wavefunction is written in terms of Slater determinants (and not CSFs), it may contain any given spatial and spin symmetry. The choice of the orbitals entering the active space is still not a trivial task. Obtaining an appropriate active space requires chemical intuition, experience, as well as some trial and error. Ideally, it should be large enough to describe all regions of the PEH that characterizes the chemical process under study on the same footing as well as all the different excited states present in a molecular system, which are typically characterized by a different degree of electronic correlation. It is troublesome, though, that different nuclear configurations (or different excited states) can sometimes be obtained with different sets of orbitals. Hence, efforts have been devoted to implement CAS CI methods based on robust active spaces. An example is the floating occupation molecular orbital CASCI (FOMO-CAS CI) method,^[50] which generates the orbital space by solving a single-determinant HF equation with fractional numbers, avoiding the orbital optimization of CASSCF and its inherent difficulties. Preliminary results of FOMO-CAS CI compared with CASSCF indicate a good performance for $\pi\pi^*$ excitations in small organic molecules, but large errors in $n\pi^*$ excited states.^[50] It seems therefore that further test calculations might be necessary before analytic gradients and nonadiabatic coupling vectors are formulated and then FOMO-CAS CI can become an extended method to study photochemistry.

In general, the correlation energy^[51] added by the description of the wave function made of several configurations is named static, non-dynamic or long-range correlation energy and, depending on the system and the nature of the electronic states, represents an important fraction of the total correlation energy, but not all of it. Unfortunately, it is hard to obtain spectroscopic accuracy when dealing with excited states because the effects of the correlation can be strongly differential. Configurations included in the CAS expansion should in principle be only those involving strong electron correlation (non-dynamic) effects, leaving for further approaches the recovering of the remaining dynamical or short-range correlation effects. In practice only the CASSCF approach has been shown able to provide balanced configurational spaces. However, since there are technical limits in the size of the CAS space (14–18 orbitals/electrons or equivalently a few million CSFs) due to the size of the generated density matrices, it is often not possible to address problems that require large reference spaces, such as extended π systems, transition metal compounds, organometallic complexes, and so forth. To alleviate these limitations, and based on the same grounds as CASSCF, a new technique was designed some years ago by Roos and coworkers^[52,53] that allows extending the number of active orbitals by restricting the CI excitation level, namely the restricted active space (RAS)

SCF method. The active space (including natural orbitals with fractionary occupation) is divided in three subspaces: RAS1, RAS2, and RAS3. Whereas RAS2 keeps the same meaning as in CASSCF (involving a CAS CI) the RAS CI is built by restricting the number of holes in RAS1 and particles in RAS3, typically two or three. An approach that lies in between CASSCF and RASSCF theory is the SplitCAS.^[54] In the SplitCAS the active space is split in two parts, a principal space and a much larger extended space, allowing for a large reduction of the storage and computational demands of the wavefunction optimization. Other techniques aimed to extend the active space based on two-electron reduced density matrices are presently under development.^[55]

When computing electronic excited states as higher solutions of the Hamiltonian, one has to assure the orthogonality of the wave functions. In CASSCF or RASSCF this is achieved by simultaneously obtaining several states that belong to the same symmetry into a state-average (SA) CASSCF or RASSCF calculation, where a functional of energy is defined as an average of a certain number of states with an associated weight. From a SA-CASSCF calculation one obtains a set of average orbitals and a number of orthogonal wave functions equal to the number of roots used in the average process. In this manner, it is for example sometimes possible to overcome the problem of "root flipping", that is, the interchange of roots along the CASSCF optimization procedure, or the collapse of the different wave functions. For a given spatial and spin symmetry, the treatment of excited states is preferably performed by using SA-CASSCF calculations because the states are then orthogonal to each other. In principle, it is also possible to make a single CASSCF calculation for each of the roots individually, optimizing just one state at a time. This is not, however, a recommended procedure, considering that the resulting wave function is very often strongly contaminated with the contributions of the other states. It is certainly not recommended in the case of electronic near-degeneracies. It cannot be recommended either to perform different calculations varying the relative weights of the states to prevent one from obtaining erratic results.

It should be kept in mind that with all the advantages, the MCSCF description is not good enough to obtain spectroscopic accuracy because large part of the effects of the correlation are missing (dynamic correlation) and, furthermore, they are strongly differential. The remaining short-range correlation energy effects, or dynamic electron correlation, have to be added on top of a MR wave function. As the addition of the dynamic correlation is expensive in any case, it has been (and still it is) a common practice to use CASSCF to provide optimized geometries for minima, transition states or Confs. A large number of photochemical studies have been performed just at the CASSCF or RASSCF levels, claiming, or hoping, that those approaches would include balanced correlation effects. Unfortunately, this is often hardly the case. Imagine a Conf involving two different states, characterized and optimized at the CASSCF level of theory. When the remaining correlation effects are included, it may well happen that the states (those forming the CASSCF Conf and others) are affected by electron

correlation in a totally different way. As a result, the Conf can move to other geometries or relate two different states, as already proven in several cases.^[56,57] Many PEHs (and derived) that are based only on CASSCF calculations can be found in the literature. Figure 1 illustrates the representation of the differential correlation problem in a typical quantum-chemistry protocol, CASPT2//CASSCF, in which using the Pople nomenclature the electronic energies are computed at the higher level, CASPT2, and the geometries at the lower level, CASSCF. As a matter of fact, the example can be extended to many type of protocols: MRCI//CASSCF, CC//MP2, CCSD(T)//CCDS, and so forth, with the same fatal consequences.

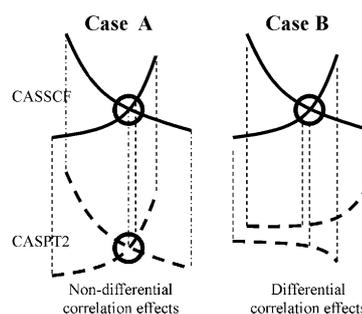


Figure 1. Effects of the correlation in a case of PEH crossing for the CASPT2-(energies)//CASSCF(geometries) protocol.

There are three basic MR approaches applicable to compute dynamical correlation effects. The MRCI method is a highly accurate procedure in which singles, doubles, triples, ... and n -tuple CI excitations are included in the final wave function. Apart from the fact that the CI expansion becomes immediately unaffordable, and the method therefore is applicable only to relatively small systems, the MRCI has another disadvantages, such that it is not size-extensive, and further corrections such as Davidson or MR-SC²CI have to be added.^[58] Another size-extensive modification of singles and doubles MRCI is the averaged coupled pair functional (ACPF) theory.^[59-61] The combination of the MRCI method with the recently developed Cholesky decomposition technique to reduce the cost of the handling of the two-electron integrals is expected to increase the range of applicability of this methodology. Efforts to reduce the cubic-to-quartic scaling of singles and doubles MRCI to linear scaling using local correlation and integral screening have been presented recently.^[62,63] Another approach that has awoken high expectations is the MRCC (MR coupled cluster) method. The presence of a multiconfigurational approach is expected to avoid the need of including high excitation orders into the CC expansion, leading then to accurate results at lower costs. Whereas efficient algorithms have already been under development for a long time, the initial results are not very promising because the contribution of the computationally expensive triple excitations seems to be required.^[44,64,65] More useful and practical are the MRPT (MR perturbative) approaches. Among them, the CASPT2 method of Roos and coworkers, based on second-order Møller–Plesset perturbation theory applied on a CASSCF reference wave function has been

the approach with more followers. After an initial unsuccessful formulation in 1981, the final CASPT2 method^[66–68] implemented in MOLCAS became the most efficient and balanced MRPT approach, reducing not only the computational cost, but yielding remarkably low size-extensivity problems, unlike other CASPT2 implementations.^[68,69] Very recently, an extension of the CASPT2 method has been developed to include RAS references, that is, the so-called RASPT2 approach,^[70] which, properly employed, allows extending the number of problems within reach by considerably increasing the size of the active space.^[71]

Regardless of the procedure employed—be it CASPT2 or RASPT2—both share a number of shortcomings. First, perturbation theory is plagued with the intruder state problem. If the reference space is not properly defined for the process under scope, the perturbative expressions will cause discontinuities in their contributions to the second-order energy (small denominators computed as orbital energy differences). Therefore, a low weight for the reference wave function will be obtained. In most cases the solution implies that new orbitals (inactive or secondary) should be added into the active space. This is easy to say, but most of the times impossible to realize computationally. Sometimes the requirement comes from the true contribution of the corresponding CI to the final wave function, but not always. The use of largely diffuse basis sets (ANO, aug-cc) often generates diffuse orbitals that may weakly couple with the computed wave function and yield spurious interactions. Efficient level-shift dumping methods (LS-CASPT2 or IMAG-CASPT2) have been developed to prevent such cases.^[72,73] The use of the imaginary level-shift approach yields the most accurate and stable solutions.^[73] A second problem is that, as corresponding to truncated perturbative expansions, the individual, single-state (SS) or single root CASPT2 or RASPT2 solutions are not orthogonal to each other and therefore there is some mixing among the states of equal symmetry. In practice, the effects are of minor importance, except in situations such as state crossings or when valence and Rydberg functions are largely mixed at the CASSCF level.^[41] A solution to that is the MS-CASPT2 (or equivalent MS-RASPT2) method,^[74] in which an effective Hamiltonian matrix is constructed where the diagonal elements correspond to the CASPT2 (RASPT2) energies and the off-diagonal elements introduce coupling to the second order in the dynamic correlation energy. The new reference wave function is formed by a linear combination of the CAS (RAS) states involved in the MS-CASPT2 (MS-RASPT2) calculation, and it has been named perturbation-modified CAS CI (PM-CAS CI). Such wave functions can be used for the computation of transition properties and expectation values at the MS-CASPT2 (MS-RASPT2) level and involve a new set of CI coefficients but the same set of molecular orbitals as in the previous SA calculation.^[74]

Despite all the beauties, it is fair to say that the MS-CASPT2 method does not always yield the best result. In the asymmetric effective Hamiltonian matrix the off-diagonal elements that couple the different states should be small and similar. Otherwise, the average process carried out for such elements may lead to unphysical results in both the MS-CASPT2 energies and the eigenfunctions. This condition can be achieved by enlarg-

ing the active space, which implies a redefinition of the zeroth-order Hamiltonian. Large active spaces, beyond the main valence MOs, are used naturally in the simultaneous treatment of valence and Rydberg states, where the MS-CASPT2 approach has proven to be extremely useful. Especial caution has to be exercised, however, for the computation of a crossing point between two surfaces, as in the case of ConIs (and avoided crossings), crucial in photochemistry (see the discussion in ref. [57]). The use of the MS-RASPT2 method may surely solve some of the problems, as recent benchmark studies show.^[71]

2.3. Methods Based on Density Functional Theory

The most popular extension of density functional theory (DFT) to the calculation of excited states is the time-dependent DFT (TD-DFT) approach (the name is unfortunate because no time dependency is accounted for in the electronic problem). This method is commonly employed because of its simplicity and apparent black-box behavior, in particular for large systems out of reach from the more accurate *ab initio* methods.^[75,76] Based, as the propagator methods, on the solution of the frequency-dependent polarizability equation,^[77,78] the procedure avoids the calculation of the explicit state just by obtaining the excitation energy and the transition dipole moment. As for any other single-reference approach, the adequate application of the method is typically restricted to structures which have closed-shell ground-state references. Apart from that, and as for any other DFT approach, the behavior of TD-DFT relies on the frequently erratic performance of the heavily parametrized functionals. The procedure can be, however, generally applied to study simple absorption and emission spectra, provided that an accuracy below 0.5 eV is not required. Otherwise, the flaws of the method/functional are well known: poor description of charge transfer (CT) states,^[79,42] lack of multiconfigurational character^[79] and doubly or highly-excited states, together with very large and systematic errors in valence states of large π -extended systems (especially related to the poor description of charge localized situations),^[80–82] and the impossibility to cope with degenerate situations such as ConIs.^[57] In dramatic cases the deviations can be as large as 5–6 eV^[83,84] or the particular state may not even exist.^[83]

Despite the great effort devoted to find functionals able to compute all types of excited states in a balanced and accurate way, the truth is that present-day TD-DFT excited-state chemistry involves a series of ad hoc functionals and corrections used independently by research groups for different purposes and situations: empirical dispersion corrections,^[85,86] long-range corrections to deal with CT or Rydberg states,^[87–89] broken-symmetry approaches,^[90–94] inclusion of the Tamm–Dancoff approximation for degeneracy situations,^[95,96] and so forth.

Even if the overall accuracy of these methods has improved much since the early times and its black-box applicability has slightly increased, it is still questionable whether they will ever have high accuracy and, especially, predictability, as required in photochemistry.^[84,98–100] The obvious question remains: how does one improve the results when using DFT functionals and how does one obtain results of predictive power? Unfortunate-

ly, the behavior of TD-DFT for excited states is much less satisfactory than that of standard DFT for computing ground-state properties.

As stated above, in general, TD-DFT calculations can reach an accuracy of 0.5–0.4 eV. More striking is the description of CT states. Since throughout the manuscript we deal with CT states and there is an increasing effort from the DFT community to develop exchange–correlation (xc) functionals capable to increase the spectroscopic accuracy by using TD-DFT methods, we introduce in the following the new xc functionals developed with this purpose. CT states are usually underestimated due to the incorrect long-range behavior of the current standard xc functionals. Thus, CT states with TD-DFT do not exhibit the correct $1/R$ profile along a charge-separation coordinate R .^[12,101] Spurious solutions with errors amounting to a few eV might be obtained in some situations, therefore a pre-examination of our molecular system and the available functionals is required. In this sense, pure functionals are specially affected to properly treat CT states, especially in those cases where the charge-separation R is very large. Global hybrid functionals, like B3LYP and PBE0, may deal better with CT situations, specially the latter functional.^[102] Attempts to improve accuracy on CT and Rydberg situations while maintaining good quality for local excitations led to the development of range-separated hybrid functionals. Thus, short-range exchange is treated using a local functional whilst long-range exchange is mainly treated using exact orbital exchange. These schemes lead for instance to the LC- ω PBE^[103] and CAM-B3LYP functionals,^[87,88] which deal reasonably well with CT cases. Benchmark studies have been performed in azobenzene^[104] and derivatives,^[105] anthroquinone dyes,^[106] and other organic chromophores,^[102,107] demonstrating the good performance of CAM-B3LYP and PBE0 functionals to describe the excited states of organic dyes. In exceptional cases, pure functionals might describe reasonable CT states, as for example in 4-(*N,N*-dimethylamino)benzotrile.^[108,109] As later on examined by Tozer and coworkers^[88] the decent behavior of the pure functionals for describing CT states is due to a large overlapping between the occupied and virtual orbitals that are involved in the CT state. On the other hand, the recently developed *meta*-hybrid M06 and M06-2X functionals^[110] look very promising, specially the latter, to deal with all kind of excited states.

On the other hand, of particular importance is the fact that TD-DFT methods cannot describe Colns properly, which are the cornerstone of theoretical photochemistry. Furthermore, Colns involving a closed-shell singlet initial state—the most relevant ones relating the lowest excited and ground states—cannot exist in TD-DFT or any general single-reference method because the interaction matrix elements connecting the initial and response state are not included in the formulation.^[111] In other cases the result is hampered by the wrong dimensionality of the intersection space, the too rapid variation of the energy of the response states in the vicinity of the CI, and the lack of double and higher-order excitations. Recent attempts have been made to compute nonadiabatic matrix elements (NACMEs) using TD-DFT^[112,113] for uses on reaction dynamics,

but its accuracy and applicability is far from being proved. New developments are required in this area.

Alternative approaches to TD-DFT using Kohn–Sham orbitals (KSMOs) have been developed recently to study excited states. A recently presented method which seems to beat TD-DFT in balance and accuracy is the maximum overlap method (MOM),^[114] in which KSMOs are also employed and the excited states are obtained by imposing an overlap criterion to the ground-state wave function. However, the most successful and accurate procedure using KSMOs is the DFT/MRCI hybrid approach, in which dynamic electronic correlation is taken into account by DFT, whereas static correlation is included by MRCI expansions using a one-particle basis of BH-LYP KSMOs.^[83] This method has the advantage of using a multiconfigurational expansion and therefore it can describe most of the electronic structure situations unreachable for single-reference approaches, such as Colns. The procedure has been successfully applied in a number of cases,^[115–117] especially to compute intersystem crossing processes.

2.4. Summary of the Methods

Here we briefly summarize the present status of the excited-state quantum-chemical methodology in terms of their reliability and common applicability. Certainly, we use our own criteria and we restrict ourselves to mention the most commonly employed methods. It is clear that the approach used should adjust to the needs of the problem and the researcher. Carefully calibrated TD-DFT methods (the hybrid DFT/MRCI approach should be considered a different case) can provide a general, low-accuracy description of the excited state's structure. In some cases it can be even useful to help the application of more accurate *ab initio* approaches. This is becoming more likely now that Cholesky-based techniques have expanded the applicability of *ab initio* methods to larger systems.^[70,118–121] CIS-derived methods cannot be recommended in practically any situation. Propagator approaches can, however, provide a qualitative picture of the spectroscopy, although they might fail to describe complex situations. Coupled-cluster approaches, provided that triple excitations are included, give a very accurate account of many types of excited states, but typically only near equilibrium geometries, and always when the ground-state description is not multiconfigurational, as it is the case of biradicals, Colns, dissociations or in multiexcited states. Multiconfigurational methods of the MRCI or CASPT2 type are still required to solve the latter cases, as long as the reference space can be properly defined. This is the particular situation of photochemistry, where the description of Colns is a purely multiconfigurational problem. It is important to mention that for a method to be actually useful, it must be able to provide not only electronic energies, but also molecular properties, and to offer necessary tools such as geometry optimizers or wavefunction analyzers. Many efforts have been done to obtain accurate molecular properties using response theory with propagator approaches, CASSCF or CC. Analytical gradients for structure optimizations can be found at the CIS, TD-DFT, CASSCF, CASPT2, MRCI, and CC levels of calculation.

Not surprisingly, a revision of the literature on the field of excited states in the last four years indicates that at a large number of studies use the TD-DFT methodology (see Figure 2 for an illustration of the use of the different methods in recent literature). Half of papers devoted to absorption and emission processes of medium to large molecules employ TD-DFT and proton/hydrogen transfer is also a favorite topic studied with TD-DFT. Obviously its availability in many packages, low cost and apparently black-box behavior is especially attractive for many researchers. However, it is also true that in some cases the method is applied without a clear knowledge of its limitations—for instance, when standard functionals are used to compute CT transitions. It is not unusual to find routine TD-DFT studies yielding as the lowest excited state one with CT character, a meaningless result (even if correct), considering the systematic tendency of the methodology to provide too low CT states. Photodissociation is also a slippery ground for TD-DFT and yet about 25% of case studies are investigated with TD-DFT. Biradical species cannot be described with a single configuration, so it is not surprising that often the zwitterionic character of a molecule is artificially enhanced, or discontinuities in potential energy profiles are found. Especially in this type of studies there is room for more sophisticated CASPT2 or CC calculations, notably in small systems. Also in purely photochemical reaction studies TD-DFT is widely employed, despite its well-known inability to deal with degeneracy problems and CoIns. In most cases CASPT2 is, however, the preferred method, with the MRCI approach being also employed for smaller molecules. Other methods like DFT/MRCI (frequently accurate) or SAC-CI can be also found widely spread in the literature. It is interesting that despite its known

pitfalls CIS is still comparably used to study photoisomerization, photostability and spectroscopic problems.

3. Selected Applications

3.1. Basic Spectroscopy and Photophysics in Organic Systems

Many excited-state problems addressed by quantum chemistry are purely spectroscopic, that is, they involve the study and assignment of absorption and emission band positions and intensities, as well as state properties such as charge distribution or computation of radiative lifetimes. These phenomena are considered to be the realm of photophysics. Within the spirit of the Franck–Condon (FC) principle, vertical absorption and emission energy differences are theoretically comparable to the absorption and emission band maxima, respectively. Since the calculation of emission energies implies to find minima in the excited state, and this involves complex optimization algorithms, this type of calculations are difficult, time-consuming and require more specialized methodologies than the computation of the absorption spectra. This explains why many spectroscopic studies on large systems focus only on absorption.

In general, most of the spectroscopic molecular problems can be solved by computing few structures of the PEHs of the system. This is not always an easy task, considering that one has to deal with many classes of excited states: valence, Rydberg or multipole-bound anionic states, optically allowed (bright) or forbidden (dark) states, and covalent, ionic, or zwitterionic states. The basic spectroscopy of organic systems is mainly based on valence states. Rydberg transitions typically

lie very high in energy and are not important in the low-energy range of the UV spectrum. However, when the Rydberg and valence states are close in energy, excited states of intermediate nature, valence-Rydberg states, come out quite often from the computation. To elucidate whether those states actually correspond to real spectroscopic states or are just an erroneous consequence of the truncated level of theory employed is not an obvious task. In order to discern, flexible enough basis sets have to be supplied, employing high-level methodologies with inherent flexibility to overcome the possible erratic valence-Rydberg mixing. The MS-CASPT2 method in conjunction with ANO-type (valence and centered diffuse) basis set has been proved to be an appropriate approach for an accurate descrip-

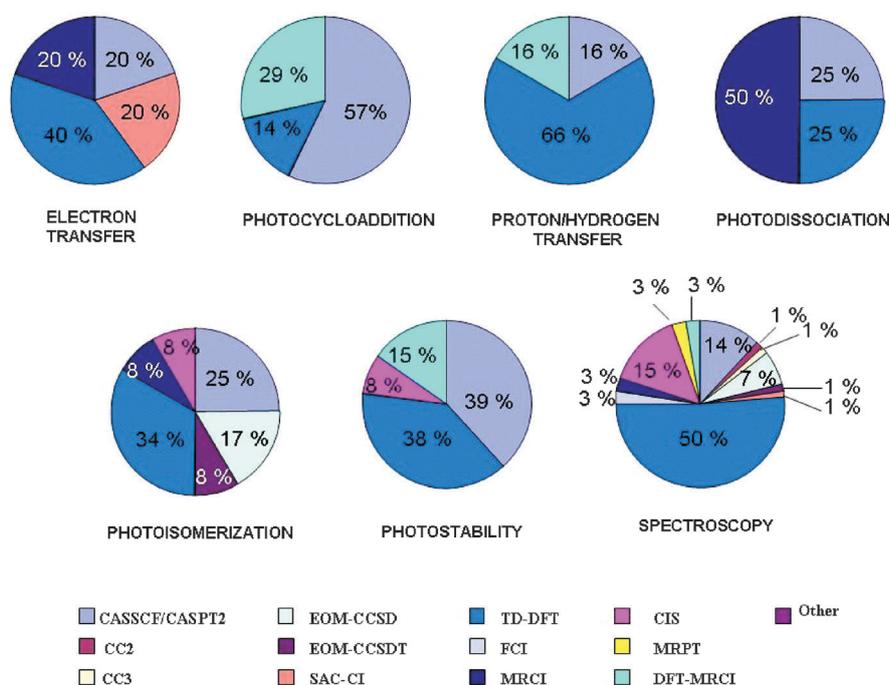


Figure 2. Studies found in the literature on molecular processes taking place in the excited state distributed by the different quantum chemical methods employed. The search parameters were “excited states” and “quantum chemistry” in the period 2007–2010. 106 papers are considered.^[122]

tion of these situations. Experience shows that valence-Rydberg mixing found in vertical transitions is in most cases spurious and it progressively vanishes upon increasing the level in the treatment of dynamic correlation.

An exemplary case that illustrates the erroneous contribution of valence-Rydberg mixing can be found in 1,1'-bicyclohexylidene.^[123] During the last two decades a number of quantum chemical methods have been employed to assign the UV absorption spectrum of this molecule, which intriguingly shows two absorption bands instead of one, as it should be expected in an olefin. The controversial conclusions reached in these studies are biased by the level of theory employed. In particular, the most recent studies based on the use of CIS and basis sets with more and more diffuse functions coalesced in an explanation based on Rydberg-valence mixing. This mixing clearly disappears when adequate basis sets in conjunction with MS-CASPT2 are employed.^[123]

An example of a system where valence-Rydberg mixing is not spurious is the water molecule. A recent accurate theoretical study reveals a natural (not spurious) valence-Rydberg mixing of the lowest-lying electronic excited states.^[124] This is an example of the so-called Rydbergization—the change in the nature of the state from valence to Rydberg with the internuclear distance—as first introduced by Mulliken.^[125] In cases like this, it is essential to assure the description of the ground and excited states with high accuracy, because then only a few points along relevant dissociation coordinates are needed in order to assign the electronic absorption and emission bands. In this context, the description of valence excitations from for example π to σ^* orbitals in which dissociation takes place, is also critical.^[126] These excitations are sometimes confused with Rydberg transitions because of the diffuse character of the σ^* orbital. $\pi\sigma^*$ states are dark but it can be populated via internal conversion and therefore can also play an important role, not only in water but also in other heteroaromatic molecules, such as ammonia, DNA, or hydrocarbons.^[126, 127]

3.2. Transition-Metal Photophysics

The study of the photophysical and magnetic properties of transition metal complexes using computational photophysics and computational photochemistry is nowadays accepted as the complementary tool to absorption and emission spectroscopy with or without polarized light, magnetic circular dichroism (MCD), Mössbauer spectroscopy, circular dichroism, or Raman spectroscopy, to mention some of the most important experimental techniques. That said, it is fair to add that the study of (very often) open-shell transition metal systems is still a challenging purpose, and particularly more difficult than organic and main group chemistry. In general, the main challenges of studying organometallic complexes include:

- 1) Dynamic correlation effects. As in organic chemistry, dynamic correlation is compulsory to achieve a quantitative comparison with the experiment.
- 2) The size. Metal complexes are typically large, involving many atoms and electrons, and therefore computationally very demanding.
- 3) State degeneracies. Degeneracies play an important role in transition metal complexes, and not just between electronically excited state potential energy surfaces (e.g. in the case of CoIns or singlet–triplet crossings) but also between near-degenerate electronic ground states. In the latter cases, the HF wavefunction will likely fail to predict the correct ground state, hence making it a bad guess for post-HF correlated methods. Hence, single-reference methods are often unreliable for transition metal complexes even to describe qualitatively the order of the electronic states. These situations make compulsory the use of a MR wavefunction, including non-dynamic correlation. This fact is a great shortcoming, since as discussed in Section 2.2, MR methods are very demanding and certainly not a black box.
- 4) Relativistic effects. These are especially relevant in organometallic complexes. The most important relativistic effects are divided mainly into the scalar–relativistic and spin–orbit coupling (SOC) effects, which are spin-independent and spin-dependent phenomena, respectively. Beyond the four-component Dirac's theory, which may be in principle combined with a multiconfigurational wavefunction but leads to lengthy and complex calculations, it has been seen that quite accurate results can be obtained transforming the four-component Dirac operator into a two-component form. Thus, one of the transformations most used today is the second order Douglas–Kroll–Hess (DKH) Hamiltonian.^[128–130] The DKH Hamiltonian can be divided into a scalar part and a SOC part. The scalar part can straightforwardly be included in a non-relativistic treatment. It includes contributions to the one-electron Hamiltonian, by introducing the mass–velocity term which modifies the potential close to the nucleus. The scalar relativistic effects dominate for the first row transition metal compounds. Conversely, for late transition metal compounds as well as lanthanides and actinides, SOC effects are more important the heavier the metal atom is. The calculation of SOCs are indispensable for the correct interpretation of many spectroscopic phenomena, such as intersystem crossing rates, MCD intensities, g-tensors, intensities in forbidden transitions, zero-field splitting, etc. Within the DKH Hamiltonian, there is a true two-component term, which mainly accounts for the SOC effects. As a two-electron operator, it is quite difficult to implement for molecular systems. However, the development of effective one-electron Fock-type spin–orbit Hamiltonian^[131] simplified the algorithm for the subsequent calculation of spin–orbit matrix elements. The DKH Hamiltonian is operative with the CASPT2//CASSCF framework in combination with relativistic basis sets (ANO-RCC) and the atomic mean field integrals (AMFI) approach^[132] that avoids the calculation of multi-center integrals reducing the computational effort, for example in the MOLCAS quantum chemistry software.^[133]

compound] have been extensively studied with different theoretical methods.^[171] Herein we do not focus on the effect of substitution of the $[\text{Cu}_2\text{O}_2]^{2+}$ core—for this the reader is referred to ref. [171] and references therein. Instead, we only discuss the results concerning the A–B energy splitting obtained with different methods.

In compound B the copper is in the formal oxidation state of $2+$ (d^9 electronic configuration) whilst in compound A it is $3+$. Thus, in the case of compound B one could think that both d^9 copper atoms couple ferromagnetically, that is, generating a triplet spin state, or antiferromagnetically, that is, generating a singlet biradical. Experimentally it is shown that B has a singlet ground state, thus pointing to a biradical character. Recall that singlet biradicals cannot be represented with a single Slater determinant and therefore are complicated to describe by monoconfigurational methods. Such a deficiency can be overcome with post-correlated CC methods allowing up to triple and even quadruple excitations in conjunction with a large basis set. Indeed, the completely renormalized (CR)-CC level of theory, including triple excitations, the rigorously size-extensive CR-CSSD(T)_L model,^[172] predicts the correct energy splitting between the A and B species.^[173,174] The local pair natural orbital CC method, that is, LPNO-CCSD,^[175] in conjunction with complete basis set extrapolation, triple excitation contributions and relativistic effects is also accurate.^[176] As we state above, antiferromagnetic situations are one of these specific cases where DFT should be carefully applied. And this is the case of compound B. Hybrid functionals underestimate the stability of the isomer A, with an underestimation proportional to the amount of HF exchange. Accordingly, only pure functionals, such as BLYP, yield accurate relative energies of A–B. However, no single functional seem to be well-suited to accurately describe all the reactive schemes between the three species shown in Figure 3.^[173,174]

Fair to say, the application of multiconfigurational schemes in these systems is also very challenging. The CASPT2(16,14) study of Cramer and coworkers^[173] significantly overestimated the energy of A, giving quantitative discrepancies with the CR-CSSD(T)_L results. The employed active space, while on the edge of computational feasibility, was not able to handle all the electron correlation. The complete valence space for the $[\text{Cu}_2\text{O}_2]^{2+}$ core (32,20), including the copper 4s and 3d orbitals and the oxygen 2s and 2p orbitals, plus the double-shell effects of 10 additional 4d orbitals, is clearly beyond the limit of CASPT2. Recently, Gagliardi and coworkers have applied RASPT2(24/28) to the system, finding a good agreement with the CR-CC results.^[166]

$[\text{Cu}_2\text{O}_2]^{2+}$ is also a good scenario to evaluate relativistic effects. Although copper is a 3d transition metal atom, relativistic effects are important and favor the B isomer. Both the ZORA and DKH methods performed equally and they are preferred to the quasirelativistic ECP, which account only for half of the total relativistic contributions.^[176]

3.2.2. Excited-State Description of Transition Metal Complexes

In the last years many excited states of transition metals have been obtained using MR methods, especially with the CASPT2//CASSCF protocol, but in comparison to TD-DFT calculations, the number is still small because it is pragmatically unaffordable for large molecules. As in other playgrounds, the RASPT2 protocol will be a good alternative for studying excited states in transition metal complexes in the near future.

In line with the recent development of MR approaches and the enormous increase in computer power in the last decades, the interest in the calculation and interpretation of transition metal optical spectroscopy has evolved to a more ab initio oriented problem. The work of Neese et al. aimed at the development of the spectroscopic oriented configuration interaction (SORCI) method is a good example.^[177,178] This method is based on concepts of individual selection^[45,179–181] and difference dedicated CI (DDCI)^[182] and can achieve great efficiency through the combination of variational and perturbational theory. All in all, it is a simplified MR method for the calculation of excitation energies and optical as well as magnetic properties. The SORCI method has found large resonance in the last years for medium-sized molecules.^[163,169,183–186] Further attempts to get a compromise between computational effort and accuracy led in the past to the development of semiempirical methods. An example is the spectroscopically parametrized intermediate neglect of differential overlap technique (INDO/S), which combined with CIS has been also applied in transition metal spectroscopy.^[187–190]

In the following we discuss the main photophysical properties of transition metal complexes, the specific performance of all the methods stated above (its pros and cons) and the future perspectives in this field. Concerning UV/Vis studies, historically the beautiful colors that coordination complexes exhibit have attracted the interest of the scientific community because important information about ligand field theory, coordination number and spin configuration, as well as ionicity/covalency of the ligand–metal bond, can be extracted. Mainly five types of electronic transitions are found in coordination chemistry.

1) d–d electronic excitations. They are in principle strictly not permitted by Laporte rules in centrosymmetric environments but partially allowed due to vibronic and spin–orbit couplings and thus, exhibit generally lower extinction coefficients than CT transitions. These ligand-field (LF) excitations are responsible for example for the blue color of Cu^{II} water solutions.

2) ligand-to-metal CT (LMCT) excitations. They involve promotion of electrons from occupied ligand orbitals to the partially empty d shell of the metal. Such transitions are responsible, for instance, for the intense purple color of the permanganate anion.

3) metal-to-ligand CT (MLCT) excitations. These transitions involve excitations from metal d-based orbitals to low-lying empty orbitals located on the ligand, typically of π^* character.

4) intra-ligand (IL) transitions, involving excitations between ligand-based orbitals which are located on the same ligand.

They are usually present in the UV/Vis spectrum of the ligands without complexation.

5) ligand-to-ligand CT (LLCT) states. These transitions involve ligand-based orbitals, with the orbitals located in different ligands.

Different methods behave differently while simulating the different electronic excitations. We note that in transition metal complexes many of these excitations fall typically into the UV/Vis region. Let us begin the discussion with the LF excitations. It has been seen that to describe LF transitions MC methods outperform the rest of *ab initio* and TD-DFT methods.^[178] Even though TD-DFT succeeds to describe the LF states of several closed-shell transition metal carbonyl complexes,^[191] Neese and coworkers have pointed out the drawbacks of TD-DFT for describing d–d transitions of open-shell transition metal complexes, especially in problematic configurations, like the d^8 situation. This is for example, the case of the octahedral $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ complex, for which extensive studies have been done.^[178] For this compound, TD-DFT exhibited errors exceeding 5000 cm^{-1} and was not capable of predicting the correct number of d–d transitions. The reason for this failure is that some LF states contained substantial double excitation character, which TD-DFT cannot handle within the constraint of the adiabatic approximation. The SORCI method shows very good behavior while dealing with LF excitations regardless the d configuration.^[178] Precisely in the $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ complex, the effect of SOC on the absorption spectrum have been evaluated.^[178] Calculations were carried out at both the SORCI and SA-CASSCF level of theory. SOC introduces a shift in the main states of the order of a few hundred wavenumbers. Furthermore, inclusion of SOC leads to the splitting of the ^3T states, and hence perfectly matching the experimental evidence. For further details we refer the reader to ref. [178].

Concerning CT transitions (either LMCT, MLCT, or LLCT), work done with *ab initio* MC methods is scarce, since the complexes very quickly exceed the size that can be handled computationally. Here we note the remarkable work of Daniel and coworkers in elucidating the electronic absorption characteristics of different transition metal complexes using CASPT2, see for example refs. [191–196] A good agreement with experiment was found for the MLCT transitions of typical carbonyl complexes,^[193, 194, 196] as well as in other type of complexes.^[161] Unfortunately, CASPT2 calculations are not possible in systems like $[\text{Ru}(\text{bpy})_3]^{2+}$ or $\text{Ir}(\text{ppy})_3$ and related complexes, which are prone to act as light-harvesting antennas in photochemical devices, like in artificial photosystems and OLED technology, respectively. Due to the presence of many low-lying π^* conjugated orbitals located on the ligands (giving rise to the MLCT transitions) and the typical covalent metal–ligand bonds of such complexes, very large active spaces are required. Additionally, the correlation shell for the d orbitals is necessary. This makes even RASPT2 calculations challenging. As a consequence, this type of molecules has been the typical target for TD-DFT calculations. In general, it is only the experimental UV absorption spectrum or emission energies that are compared with the theory. Our work on Ru ,^[197–200] Ir ,^[201, 202] Pt ,^[203, 204] and Zn ^[205] complexes, and that of many other groups, see for ex-

ample refs. [206–209], have found that, astonishingly, TD-DFT can be in reasonable agreement with the experiment as long as a judicious selection of functionals/basis is done and solvent effects are included.^[198, 202, 206] A recent study on the *trans*(Cl)- $\text{Ru}(\text{bpy})\text{Cl}_2(\text{CO})_2$ complex shows that functionals bearing intermediate amounts of exact exchange, such as M06, PBE0 and B3LYP, can deliver energies comparable to RASPT2 ones.^[210]

The question that naturally arises is, which functionals perform better in a particular situation? And what is more, are the conclusions obtained for a specific transition metal series transferable to other compounds? As we stated above, CT situations are difficult to treat with TD-DFT and specially tailored functionals are necessary for these cases. Although in some organic systems (e.g. endoperoxides^[211]) it is also possible to find transitions of very different character, this situation is very common for transition metals, making them especially complicated to treat. The simultaneous presence of different transitions contributing to the UV/Vis spectrum requires one to find a compromise among the different functional parameterizations. In a recent paper it has been stated that (as for organic dyes) hybrid functionals outperform pure functionals.^[212] Range-separated hybrid functionals perform relatively good to enable one to obtain the Q bands of several bacteriochlorophylls.^[213] Interestingly, the low-lying states of $\text{Fe}(\text{phen})_2(\text{CN})_2$, mainly of MLCT character, are described well with both pure (PBE) and hybrid (B3LYP) functionals.^[214] Moreover, the agreement in the presence of a continuum solvent or microsolvation improves slightly with the use of PBE and not the B3LYP functional. The reason behind the striking good performance of the pure functional in such a situation is probably due to the mixing of the d-based orbitals with ligand-based orbitals, leading to an overlapping of the orbitals involved in the state and a hence to a loose CT character.

In conclusion, although TD-DFT is nowadays the most popular method to calculate excited states of large transition metal complexes, a judicious selection of the functionals and basis sets should be made. Furthermore, inclusion of the solvent effects is important to get a quantitative agreement with the experiment and they must be included, especially if MLCT states are involved.

3.3. Nonadiabatic Photochemistry

In perspective, the field of computational photochemistry is relatively new in comparison to ground-state computational reactivity. Among the reasons for that are the intrinsic difficulties of following photochemical pathways after light excitation, extending expensive single-point excited-state calculations to PEHs, and last but not least, calculating properties in the surroundings of surface crossings, where the Born–Oppenheimer approximation breaks down. Here, it is useful to distinguish between adiabatic and non-adiabatic (or diabatic) photochemical reactions. Adiabatic reactions are entirely completed in an electronically excited state potential energy surface without involvement of surface crossings whilst in non-adiabatic processes at least two coupled PEHs are involved in the photochemical reaction. Following the definition of Förster, in an adiabatic

process deexcitation occurs either in the region of the reactant or of the product, whereas in the non-adiabatic case it occurs in between them.^[215] Nowadays, one speaks about surface crossings mediated by Colns to describe non-adiabatic photochemistry. It is also well-accepted that both adiabatic and non-adiabatic processes are ubiquitous in photochemistry.

The possible pathways in a typical photochemical reaction are shown in Figure 4. Upon excitation from the ground state S_0 , a singlet excited state is populated vertically (S_1 in Figure 4). After relaxation to the lowest vibrational level, fluorescence can return the molecule to the electronic ground state emitting a photon. Alternatively, radiationless processes are possible via different mechanisms that in general require surface crossings (non-adiabatic photochemistry). Surface crossings can take place between states of different multiplicity (intersystem crossing, ISC) or between states of the same multiplicity (in a process named internal conversion). If a triplet state is populated, an additional ISC with the ground state can lead to the photoproduct in the ground state, or a photon can be emitted in the so-called phosphorescence process. In principle, two types of internal conversion processes can be distinguished. One is based on vibronic coupling at the fluorescent minimum and can be relatively slow (explained with the Fermi golden rule, see for instance ref. [2]) and usually decreases the fluorescent quantum yield. The second one is ultrafast and occurs at the Coln (in Figure 4 leading to the reactant). The decay that leads to the photoproduct is not (properly) internal conversion—which usually refers to a non-reactive process—but rather a photochemical reaction.

The importance of surface crossings, or more in general of seams of intersections, is that they provide very efficient “funnels” for radiationless deactivation pathways—in the case of internal conversion taking place on a subpicosecond scale. Already in the early 30s, Teller realized that ultrafast internal conversion was due to a real touch of two potential energy surfaces.^[216] In the late 60s Zimmerman presented a reformulation of the well-known Woodward–Hoffman rules,^[217] emphasizing the importance of crossing points in the route for conversion of excited-state reactants to ground-state products in organic

photochemistry, namely in a pericyclic reaction. By that time, these models were coexisting with others where Colns were not believed to play a role in photochemistry at all, like the Van der Lugt–Oosteroff model,^[218] in which the stereochemical preference of some pericyclic reactions was predicted on basis of a small energy gap at the avoided crossings, corresponding to the disrotatory and conrotatory photochemical pathways. To be fair, we note that at that time there were no gradients available to map the excited-state energy surface and the only quantity that could be computed was the potential energy of the involved electronic states. Therefore, the authors were left to postulate a reaction coordinated that missed the Coln.

Regardless of the discussion of its real existence, in the early times Colns were thought to be extremely rare or energetically inaccessible. It was in the late 80s, coinciding with the increase of computer power as well as the implementation of gradients in the CASSCF method, that a great number of Coln geometries could be identified without the help of symmetry constraints or qualitative MO arguments. The pioneering and fecund work of Robb, Bernardi and Olivucci^[219,220] as well as others,^[221,222] proving the ubiquitous presence of Colns, not only in pericyclic reactions but in a large number of organic systems and without symmetry requirements,^[223–225] can be considered without doubt as the birth of the computational photochemistry era. Nowadays, it is well-established that Colns mediate all kinds of chemical events such as bond making, bond breaking, hydrogen transfer, isomerization, CT or group exchange.^[226–228,97] Figure 5 illustrate the number of photochemical reactions assisted by Colns found in the literature for distinct topics. The traditional pericyclic reactions field has been exhaustively worked out, closely followed by proton/hydrogen transfer or *cis/trans* isomerization reactions, but the number of optimized Colns in other type of reactions is also not negligible. A current field of research where Colns play an important role is the understanding of the deactivation mechanisms of DNA bases after sunlight activation. Once DNA is ex-

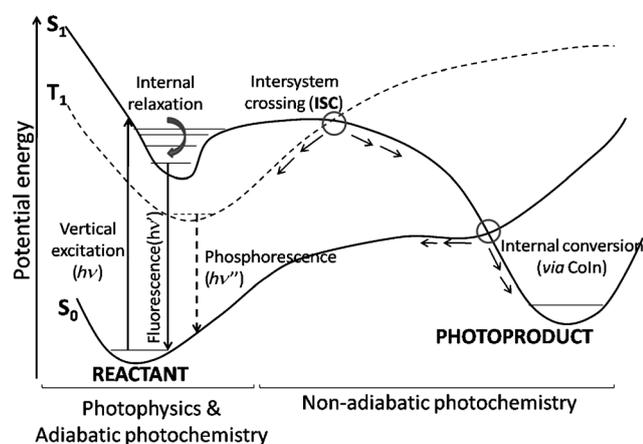


Figure 4. Main adiabatic and non-adiabatic processes in photochemical processes

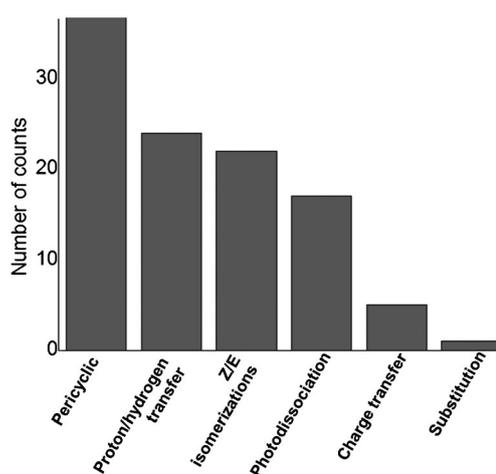


Figure 5. Studies found in the literature on Coln divided by topics. The search parameters were “conical” and refinements were done by “chemistry” and “reaction”. 346 papers were obtained, among them only those where Colns are explicitly provided (114) are considered.^[122]

cited, Colns are responsible for the efficient internal conversion channels that recover the ground state reactants in an ultrafast manner (fs time scale) without a photochemical transformation. These deactivation channels are one of the main mechanisms that nature uses to avoid lesions and mutations in DNA. Further reading on computational photochemistry and Colns can be done in refs. [229–231].

At a Con vibronic coupling allows for population transfer between (typically) two electronic states. In the crossing regions there are two important modes that form the branching^[222] or **g,h**^[232] plane of the reaction, along which the degeneracy is lifted. These modes are defined by the gradient difference (**g**) and the interstate coupling (**h**) vector. A three-dimensional PE surface plotted along these two modes provides the typical double inverse cone shape (Figure 6a).

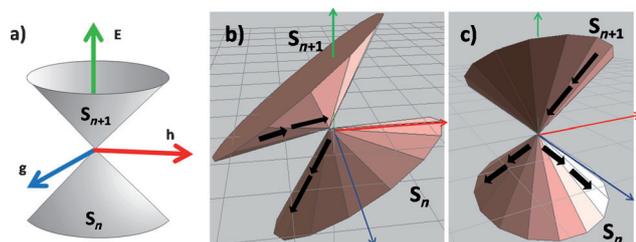


Figure 6. a) The branching or **g,h** plane of a Con. Representation of b) sloped and c) peaked conical intersections.

Different classifications of Colns are possible, attending to the electronic state symmetry, the topography, or the dimension of the branching space.^[233] According to the symmetry of the electronic states involved, Colns can be *required by symmetry* if the two states belong to a degenerate irreducible representation or they can be *accidental* if they do not. In the latter case, the two states can have distinct (*accidental symmetry-allowed*) or the same (*accidental same-symmetry*) spatial symmetry. Among them, the most difficult to optimize are the accidental same-symmetry Colns because a priori there are no hints about the nature of the molecular structure. For its localization we are therefore mostly left to an efficient optimization algorithm. Since such intersections are permitted in a seam or intersection space of $N^{\text{DOF}}-2$ dimensions, where N^{DOF} is the number of internal degrees of freedom, the larger the molecule, the most critical is the use of a reliable optimization algorithm and a pinch of chemical intuition to find the Con. Further help can be provided with the intuitive method provided by Zilberg and coworkers that, based on the Longuet-Higgins phase change theorem, is able to predict the location of Colns between (typically) the ground and the first electronic state.^[234,235] According to the topography, Colns can be classified into *sloped* (Figure 6b) and *peaked* (Figure 6c).^[222] A sloped crossing is characterized by two approximately parallel gradients and two minima of the respective crossing states lying on the same side of the crossing. A peaked crossing shows almost orthogonal gradients and two minima at each side of the crossing (typically reactant and photoproduct). In a

very simplified manner and without taking into account dynamic effects, one should expect a greater branching of photo-product/reactant ratio for the peaked crossing situations. Finally, Colns can also be classified depending on the dimension of the branching space. Particularly relevant is the fact that Colns are not restricted to two PE surfaces. Surface crossings can also take place among a manifold of states. Symmetry required Colns involving three states have been early recognized.^[236–239] However, the presence of *accidental* Colns involving three states and its role in the photochemistry (see also Section 3.3.1) is emerging only now^[240–247] and it will be subject of intensive investigation in the coming years. Accidental Colns involving four states are much more recent.^[248,249] Three- and four-states degeneracies are characterized by a $N^{\text{DOF}}-5$ and $N^{\text{DOF}}-9$ branching space, respectively. The higher the number of states is involved, the more complicated the optimization of these points. Up to date there has been a lack of generalized algorithms able to handle the efficient optimization of a degeneracy point in an arbitrary number of electronic states.

From a computational point of view, a fair investigation of photochemical pathways requires a three-step procedure. After the characterization of the vertical spectrum and assignment of the spectroscopic state(s), one should first obtain the critical points involved in the photochemical pathway, such as minima, transition structures and surface crossings. Second, it is recommended to perform a reaction path calculation in order to confirm (in the best case) or to find out (the usual case) the connectivity between the obtained stationary points. To this aim, minimum energy path (MEP)^[250] calculations, which connect the stationary points beginning from the FC excitation and end in the ground-state products are useful. MEPs calculations are computationally very demanding since each step of the procedure requires the minimization of the PEHs on a hyperspherical cross section characterized by a predefined radius. Once the new geometry is optimized, it is taken as the center of the new hypersphere cross section of the same radius, and the iterative procedure is repeated until the bottom of the energy surface is reached. These methods were first proposed by Celani et al.^[251] and Garavelli et al.^[252] For other earlier methodological contribution also see ref. [253]. If mass-weighted coordinates are used the MEP corresponds to the intrinsic reaction coordinate (IRC)^[254] method. In complicated situations linear interpolation in internal coordinates (LIIC) path calculations may help to connect some topographically distinct stationary points.

Usually a nice qualitative picture of the photochemical process is already obtained within this two-step procedure. Nevertheless, it is useful to keep in mind that Colns are not isolated points but rather structures connected to each other in the high-order dimensional PE hypersurface. What is normally called Con is the lowest-energy point along this hypersurface. However, the knowledge and characterization of the crossing seam in different dimensions provides important additional information,^[255] but unfortunately this is not straightforward to calculate. The first attempts to map the crossing seam of an excited organic chromophore were reported by Migani et al.^[256,257] In contrast to what was believed in the early times

of computational photochemistry, this minimum-energy Con structure may not be the key geometry at which non-adiabatic transfer takes place. Thus, crossing points located higher in energy, but thermally activated, might be more accessible and then may also act as efficient funnels. Moreover, enough coupling might be present at an early stage of the seam so that the molecule escapes from the upper surface before the Con is reached.^[258] For these reasons, the third step in properly elucidating photochemical deactivation pathways should be based on obtaining time-resolved information from reaction dynamics calculations. Only a dynamic simulation can tell us which geometries are really relevant in a particular reaction and which paths are preferred. Moreover, they allow one to be quantitative with experimental quantum yields, and since the development of fs spectroscopy, with time scales. The advantage of dynamic simulations against experiment is that they allow exploring additional pathways hidden in the complex topology of the PEH, thus predicting different photochemical outcomes if particular experimental conditions are changed.

Incidentally, it is worth mentioning that before time-resolved fs experiments^[1] could confirm that internal conversion is ultrafast—as predicted in the 30s—the quantum dynamical simulations of Köppel and coworkers clearly demonstrated that depopulation to the lower state through a Con in ethylene (a prototype system which deactivates via a Con) is efficient and takes place in 10^{-14} s.^[259] Nowadays, in line with the explosion of ultrafast science in the twenty-first century, a number of strategies are readily available to complement stationary quantum chemical structures and reaction paths with time-dependent properties. Among the favorite methods to unravel photochemistry are surface-hopping molecular dynamics,^[260,261] the multi-configurational time-dependent Hartree method (MCTDH),^[262] the ab initio multiple spawning (AIMS) method of Martínez and coworkers,^[263,264] and the newly developed direct quantum dynamics method using variational multi-configuration Gaussian wavepackets.^[265] Quantum dynamics in PE surfaces of reduced dimensionality are also very useful,^[259] but require a careful analysis of the reaction coordinates which are appropriate to describe the chemical reaction. A too small number of dimensions can lead to misleading results, see for example ref. [266].

3.3.1. Photochemistry of DNA/RNA Constituents

The photochemistry of DNA is one example of beautiful complexity whose enlightenment requires the synergy of experiment, quantum chemistry and dynamics. An intriguing feature of DNA/RNA nucleobases is that upon near-UV irradiation they evidence photostability and, hence, avoid photoreactivity. This fact has an enormous relevance in biology, due to its implications in DNA photodamage.^[267] As a consequence, numerous efforts have been made to solve questions concerning the electronic excited states populated after UV light irradiation, deactivation pathways, lifetimes, influence of solvent, etc. Without the intention of being complete, because literature on DNA has become massive in the last years, we point below to

some recent publications focused on the photochemistry and spectroscopy of DNA constituents.

A good review on DNA excited states from the experimental perspective was given by Crespo-Hernández et al. in 2009.^[268] One of the authors has also reviewed the photochemistry of natural DNA/RNA base monomers from a computational sight, comparing the results with non-natural base monomers, and then shedding light on the role of natural selection in preventing photochemical damage in DNA.^[269] Another theoretical review^[270] as well as reviews concerning gas-phase spectroscopy^[271–273] and time-resolved emission experiments^[274] have recently appeared. As a general characteristic, all the natural nucleobases present in DNA/RNA (adenine, guanine, cytosine, thymine and uracil, see Figure 7) exhibit ultrafast decays that are the consequence of barrierless reaction paths beginning from the FC region—typically from the spectroscopic $\pi\pi^*$ state—and leading to Cons that bring the system to the ground state.^[275–278] Accordingly, yields of fluorescence or other adiabatic processes of single bases in aqueous solutions are very small.^[279,280] Ultrafast studies have confirmed many of these photochemical pathways.^[281,282]

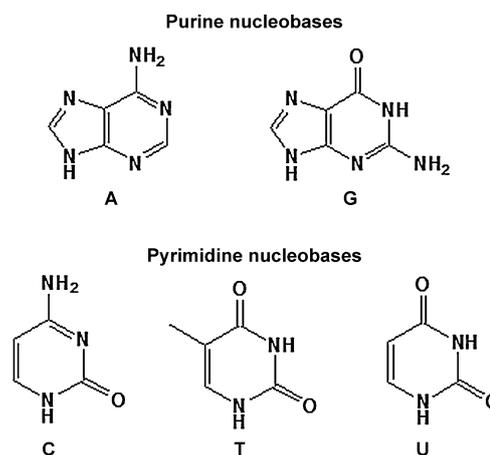


Figure 7. Purine and pyrimidine nucleobases: adenine (A), guanine (G), cytosine (C), thymine (T), and uracil (U).

An interesting question is whether the conclusions extracted for the single-base monomers can be extrapolated to DNA/RNA oligomers and polymers. It is not yet established how well the nucleobases represent DNA itself, that is, to which extent modeling two stacked bases in an orientation similar to DNA may represent the DNA molecular complexity correctly. If even methylation of nucleobases may change the excited-state relaxation pathways along the intrinsic degrees of freedom,^[269] the presence of the sugar and other components can also affect the photochemistry in ways that are still not investigated. Computationally, it is a real challenge to model systems of increasing size with multiconfigurational methods. In principle, the excited-state nature of DNA depend sensitively on base sequence and stacking but remains almost insensitive to helix conformation or base pairing.^[268,283–285] In multimers it is usually observed that relaxation to the ground state after UV excita-

tion takes place through a multiexponential decay with different lifetimes.^[283–287] Extensive computational work^[288–292] has shown that the paths for ultrafast deactivation found in the nucleobases are still open in the multimers, being then responsible of their ultrafast decay. Therefore, a large part of the initially absorbed energy will decay in sub-ps time by the same channels as those found in the monomers. Intrastrand stacked excimers/exciplexes, which are the origin of the red-shifted fluorescence observed in several oligonucleotides, as has been seen experimentally^[285,293] and theoretically confirmed^[294] and which are known to be formed mainly by stacks of two nucleobases, will be formed as well as neutral and charge-transfer dimers, which will all finally evolve to the same monomer decay channel after surmounting an energy barrier.^[288] These potential barriers are the explanation for the deactivation mechanisms that lead to the slowest transients (> 4 ps) detected experimentally.^[274] Additionally, it has been proposed that hydrogen-transfer-mediated or base tautomerism could be also responsible for the relaxation dynamics of DNA,^[295–297] although base pairing does not strongly influence the relaxation dynamics of double-stranded DNA. In any case, we can conclude that both mechanisms (mediated by the Watson–Crick hydrogen bonds and the intrinsic degrees of freedom of the nucleotides) at least compete in single base pairs, especially in the case of the guanine–cytosine pair.^[296,297]

Since, as we have discussed above, the photochemistry of DNA might be strongly determined by that of the monomers, it is worth to highlight the main non-adiabatic photochemical processes of the base monomers and the challenges that their study represent. As mentioned above, natural nucleobases absorb in the near-UV region. Photochemistry begins with the absorption to the allowed $\pi\pi^*$ singlet state. CASPT2 vertical energies are predicted^[270,298–300] at 5.02 (U), 4.89 (T), 4.41 (C), 5.35 (A) and 4.93 eV (G), in agreement with the gas-phase experimental evidence. A good agreement is also obtained for absorption energies in the presence of water using the CASPT2//CASCF protocol within the PCM method.^[270] Solvent effects are indeed important and can shift some states, biasing the vertical spectrum of the main nucleobases.^[300] In some cases the assignment of the vertical spectra in solution has generated some controversy, for example in uracil. A better description is achieved then using explicit and implicit solvation models.^[301–304] The inclusion of solvent effects in the analysis of the PEHs far away from the FC region is also worth exploring^[6,305–307] and its effect on the dynamics needs to be investigated.

Low-lying $n\pi^*$ excited states are not directly populated due to their small oscillator strengths, but can also be important in understanding secondary photochemical radiationless decays. This is the case of the nucleobases A, T, U and C. In the gas phase, the $\pi\pi^*$ state of G and C corresponds to the S_1 , unlike the rest of nucleobases. Excitation to the spectroscopic state and relaxation along its potential energy surface leads to a strong change in the bond order of some double bonds of the purine/pyrimidine ring. Consequently, twisting around the double bonds, as in the photoexcited ethylene, takes place. The excited-state energy is relatively insensitive to the ring de-

formation but the ground state is strongly destabilized due to the loss of aromaticity. Hence, both potential energy surfaces approach each other energetically, leading to a Con between the ground and the $\pi\pi^*$ state, often called the ethylenic Con because it resembles twisted excited ethylene. Indeed, MEPs from the $\pi\pi^*$ state lead barrierlessly to this Con, directly for G and C, and indirectly in A, T and U. This process is usually assigned to the fs component of the multi-exponential decay measured in DNA nucleobases.^[308,309] Ab initio on-the-fly surface-hopping dynamical simulations confirm the existence of this ultrafast path for all the nucleobases.^[310]

In A, T and U nucleobases, other Cons between the low-lying $\pi\pi^*$ state and dark $n\pi^*$ states are accessed due to out-of-plane vibrational modes of the ring, bond inversion modes, and pyramidalization modes.^[275–278,311–314] These surface crossings make the relaxation mechanism more complicated to follow. The $n\pi^*$ states involve a lone pair located in the oxygen atom for U and T and a lone pair of a nitrogen for A. The case of C is—as a matter of fact—more complicated than the path sketched above. Both lone pairs in the O and N atoms give rise to $n\pi^*$ states that depending on the level of theory have been predicted to be involved in the deactivation. Moreover, different deactivation mechanisms have been suggested in the recent years as a consequence of different basis sets, different active spaces, and different methods. Much of the controversy is based on the presence or absence of a minimum in the $\pi\pi^*$ spectroscopic state.^[247,311,312,315] For all the pyrimidine nucleobases a planar minimum is obtained with MEP calculations,^[276] but the results for C strongly change with the level of theory.^[312] This minimum has been attributed as a possible explanation^[276] for the ps time scale component of the multi-exponential decay of nucleobases.^[309]

For the nucleobases where a minimum in the $\pi\pi^*$ state is found, the barrier separating this minimum from the Con with the ground state is not only strongly affected by the inclusion of dynamic correlation, but also by the presence of solvent. Again C is a very sensitive case. A LIIC reaction path between the minimum and the ethylenic Con shows a diminished barrier amounting to only 2.5 kcal mol⁻¹^[276] when CASPT2 single-point energies on the MEP structures are computed. Solvent effects might also make the process barrierless^[306] or not,^[305] depending on the solvation model employed. Although a priori one might think that the most appropriate manner to interpret the multiexponential disputed decay of C (and other nucleobases) is to perform dynamic simulations, one should keep in mind that they are biased by the level of theory employed in the “on-the-fly” calculations. Therefore, different mechanisms have also been proposed in dynamic papers about C,^[247,310,316,317] which (at least) formally agree with the stationary paths proposed with the level of theory at which the quantum chemistry was performed.

Interestingly, besides the paths mentioned above, several three-state Cons have been optimized in C and could take part in its deactivation.^[246,318] Indeed, surface-hopping dynamic calculations confirm that a large amount of population is deactivated in C via such structures, rather than through two-state Cons.^[247] The role of the three-state Cons optimized in other

nucleobases with the help of quantum chemistry^[302,246] still remains to be investigated with the help of dynamics.

For completeness, we mention that other dynamic studies on the photochemical deactivation of the rest of nucleobases have appeared recently in the literature: adenine,^[310,319,320] guanine,^[310,321] thymine^[310,317,322–325] and uracil.^[310,317,325,326]

Up to now, we have only discussed the role of internal conversion between singlet states in the photochemistry of DNA nucleobases. Currently, there is a consensus that the triplet states are responsible of the longest component of the multi-exponential decay of monobases. It is well known experimentally that long-time signals are quenched in the presence of oxygen, yielding high yields in aprotic solvents^[327,328] Yet, several experimental evidences need rationalization, like for example, the larger quantum yields of phosphorescence than of fluorescence in monobases,^[329] the prevalence of A and T signals of DNA at lower temperatures^[330–332] or the observed wavelength dependence of the triplet state formation.^[333] To shed some light into these phenomena, the theoretical elucidation of the ISC channels is of great importance. In this direction we note the intensive work led by Serrano-Andrés^[315,334–336] and Marian.^[337]

While the size of the non-adiabatic couplings nearby the Con determines the efficiency of internal conversion between states of same multiplicity, the situation is a bit more complex when computing ISC rates. The efficiency of ISC is determined by the Fermi golden rule, which in turn depends on the vibronic SOC factors and the FC-weighted density of vibrational states. Thus, a decreasing singlet–triplet energy gap, as in the region of singlet–triplet crossing (recall Figure 4), ensures an enlarged density of vibrational states and a proper overlap of vibrational wave functions, especially of those related to low-energy out-of-plane vibrational modes which might end up in increased ISC population transfer rates.^[338] On the other hand, since these processes compete with ultrafast processes such as internal conversion, ISC is more likely to take place in regions where the molecule is trapped for a long time.^[222,339] Thus, a combination of MEP and singlet–triplet crossings calculations, followed by determination of the SOC terms and transition dipole moments at relevant geometries should be performed to get an insight into the ISC phenomena. The SOCs can be obtained, as discussed in Section 3.2, for example, with CASPT2 (RASPT2) or with a DFT/MRCI approach using SPOCK.^[340] The ongoing results indicate that three plausible singlet–triplet crossing regions can easily be accessed along the main deactivation pathway of A, T, and U.^[334] ISC rates for pyrimidine nucleobases have been also obtained.^[337] We note that cytosine and guanine showing a more stabilized $\pi\pi^*$ state in the FC region and hence not crossing with $n\pi^*$ states in the main decay pathway might not display $n\pi^*$ -mediated ISC channels.^[334] Nevertheless, they show efficient ISC channels in low-energy regions, a fact common to all the nucleobases. These results can therefore explain the experimentally observed smaller contribution of C- and G-based phosphorescence of DNA as well as the phosphorescence wavelength dependence of DNA, since some of the ISC channels might not be effective at lower excitation wavelengths.

Despite some of the conflicting issues that were shortly discussed above, the photochemistry of the nucleobases can be considered as mostly understood by means of thorough quantum chemical and dynamics simulations. Where do we go next? One of the obvious directions to follow is the detailed examination of explicit environmental effects, for instance in the frame of QM/MM calculations, as in refs. [341,342]. Another challenging perspective is the examination of the ultrafast photo-dimerization of thymine,^[343] which is one of the major causes of mutation in DNA, and which has preliminary been examined by several authors.^[344–346]

The QM/MM framework, including excited states in the QM part, is a topic worthy of a review by itself. Here we just mention that the study of photoresponsive proteins and proteins chromophores is an exciting mainstream. Colns are of vital importance to understand the photoreactivity and/or photodeactivation taking place in such systems, which on the other hand are modulated by the protein environment. Some recent results in this field are given in refs. [227,347] and references therein.

4. Conclusions

A comprehensive review of the modern methods available for calculating excited states and their application to some important topics has been presented. Quoting Bjorn Roos,^[348] “it is impossible to make any real predictions about the future developments of a research field. Exploring the unknown cannot be predicted.” Certainly, this caveat applies to the calculation of excited states, which has been a hard task from the beginning. Clearly, further developments are required. For small or medium-sized molecules, STEOM-CC methods, and the current version of CASPT2 (or RASPT2) are excellent tools which can provide good accuracy (ca. 0.1 eV in best cases). Large systems are nowadays treated with TD-DFT, whose accuracy depends on the chosen functional. Promising functionals have been developed in the last years to treat Rydberg states, CT states or dispersion effects. The challenge of theoretical spectroscopy is that very often many different states of different nature need to be described simultaneously, and unfortunately, none of the available functionals can master all trades. Depending on the problem at hand, and this always requires some preliminary prospection and trial-and-error (so, honestly said, it is not as black-box as one would desire) it is possible to find a compromise functional and reasonable (and sometimes even excellent) agreement with experiment. For the time being, TD-DFT may be the only way to study absorption and emission properties of large dimensional problems out of reach of the current multiconfigurational methods or coupled-cluster theory. However, photochemistry and photobiology can only be treated accurately with multiconfigurational techniques. A long-awaited frontier in electronic structure theory is therefore the development of linear scaling strategies for the methods able to treat excited states. Their wide applicability is still in its infancy but eagerly anticipated. In systems in which a clear partitioning into the photoactive part and an environment can be defined, for example to describe solvation, caging effects, or protein

embedding, QM/MM methods are the obvious choice, although there is still a long way until this is really straightforward for excited-state chemistry. However, in some situations it is impossible to split the level of accuracy to treat different parts of the molecule, for example, in photosynthetic photosystems, where different chromophores cohabit, in other supramolecular structures with several chromophoric catalytic centers, where energy or charge transport takes place, or in molecular machines, where the whole system has to be described at the same level of theory. The modeling of excited states in these complex systems is a challenge awaiting the development of a generation of efficient computing methods, that could very well be based on graphical processing units.

Acknowledgements

It is tragic that this review started in cooperation with Luis Serrano-Andrés and finished without him. In September 2010, he unexpectedly died in Spain at the age of 44 years. He was beloved to us and an outstanding scientist. This review is a last tribute to the many contributions he made to excited-state quantum chemistry and the many he would have liked to share with us. The Deutsche Forschungsgemeinschaft (GO 1059/6-1 and GO 1059/7-3), the Carl Zeiss Foundation (D.E.), and the Spanish MICINN and FEDER sources through projects CTQ2007-61260, CTQ2010-14892, and CSD2007-0010 Consolider-Ingenio in Molecular Nanoscience, and the Generalitat Valenciana are gratefully acknowledged for financial support.

Keywords: ab initio calculations • charge-transfer states • excited states • photochemistry • transition metal complexes

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