Electronically excited states and photodynamics: a continuing challenge

Felix Plasser • Mario Barbatti • Adélia J. A. Aquino • Hans Lischka

Abstract The purpose of this contribution is the description of the progress in theoretical investigations on electronically excited states in connection with photodynamical simulations made within the last years and to provide an outlook on the scope of future applications and challenges. An overview over excited-state phenomenology is given and the applicability of different computational methods is discussed. Both electronic structure- and dynamics methods are considered. The examples presented comprise the explanation of the photostability of individual DNA nucleobases, the photodynamics of DNA including excitonic and charge-transfer processes, the primary processes of vision and the broad field of photovoltaics, photodevices, and molecular machines.

Keywords Electronic structure · Excited states · Photodynamics · Nonadiabatic phenomena

1 Introduction

Photoinduced phenomena in molecules play an important role in many scientific and technological fields. In biological sciences, they are related to photoaging and photodamage [1–3], to vision and light detection [4, 5], to photosynthesis and light harvesting [6–8]. In technology, they are central for photocatalysis [9, 10], photovoltaics [11, 12], imaging [13, 14], photodevices, [15, 16], conventional [17, 18] and time-resolved spectroscopy [19, 20]. It would, certainly, be unrealistic to attempt examining such huge variety of fields in one review. Instead, we intend to provide an account of recent theoretical investigations, which, although restricted to a more modest variety of topics, will still illustrate a broad range of recent achievements, as well as current limitations of quantum chemical investigations of molecular excited states.

Special focus will be laid on the interactions between chromophores in p-systems, which have recently attracted substantial interest for computational studies because of many challenging questions still to be answered. Note that as a consequence of progress in computer hardware and quantum chemical algorithms, high-level quantum chemical treatment of many of the examples discussed below has become accessible only in the last years. A large number of systems of biological and technological interest exist, where interactions between chromophores play an important role. In particular, the photophysics and charge migration dynamics of DNA fragments have attracted widespread interest and many open questions remain [2, 21]. Exciton dynamics in photosynthetic complexes and other aggregates are studied to understand how the precise arrangement of the chromophores affects light harvesting efficiency and what is the role of quantum coherence [7, 22, 23]. In particular, the technique of two-dimensional
optical spectroscopy provides fascinating signatures of the quantum nature of these processes but often poses questions that cannot be answered without modeling [7, 23].

Excitonic and charge dynamics is fundamental in organic electronics. Not only migration properties of excitons and charges are of highest interest, but especially the charge separation and charge recombination steps have a crucial influence on the efficiency of photovoltaic and electroluminescent devices [24]. Another widely used application that is based on the specific properties of excitation energy transfer (EET) is the analytical technique of fluorescence resonance energy transfer, which is used to obtain time-dependent structural information on macromolecules [25].

Several physical phenomena play a role in photoexcited molecules and molecular aggregates. Electronic excitations correspond to significant changes in the electronic structure, which may in turn lead to ultrafast non-equilibrium phenomena. For a successful modeling of excited states, it is important to understand the basic physics of different classes of excited states, as well as the available computational methods and their advantages and problems with respect to the different questions to be asked. We will start in Sect. 2 by outlining excited-state phenomenology, where aside from excited states of single molecules special focus will be laid on changes that occur due to interactions between chromophores. In Sect. 3, a number of quantum chemical methods that can be used for excited states and their advantages and limitations will be discussed. Possibilities for considering dynamical phenomena and couplings between electronic and nuclear degrees of freedom will be outlined in Sect. 4. An overview of possibilities for computing excited states in dimers and aggregates will be presented in Sect. 5. Finally, Sect. 6 will feature a number of examples selected from biology and technology and special attention will be given to the applicability of different methods for these classes of systems.

2 Excited-state phenomenology

2.1 Photoinduced phenomena in molecules

Molecules can be electronically excited by irradiation at UV or visible wavelengths. The electronic excitation promotes the molecule to a non-equilibrium state, which triggers a sequence of relaxation processes. As illustrated in Fig. 1, these processes may correspond to simple vibrational relaxation on a single potential energy surface, or may involve radiationless crossings to other adiabatic states with the same spin multiplicity (internal conversion) or different spin multiplicities (intersystem crossing); alternatively, they may involve radiative transitions to other states by fluorescent or phosphorescent processes.

In any case, between the fastest processes—vibrational relaxation taking place within few tens of femtoseconds (fs), and slowest processes—phosphorescence occurring within milliseconds (ms), a span in time of more than ten orders of magnitude is found. This large variability of processes and time scales imposes, naturally, a great challenge to theoreticians, who should be prepared to employ many different approaches and methods, tailored for each special case.

Theoretical investigations of molecular excited states usually start with the determination of the vertical excitation spectrum for the ground-state minimum geometry and continue with the determination of geometries and energies of excited-state stationary structures, of coupling terms for state crossings, and of reaction pathways connecting all those structures. In comparison with ground-state research, excited-state investigations impose a new level of challenges due to the high density of closely lying states possessing different delocalization character (localized valence states, delocalized excitons, separated charge-transfer states, diffuse Rydberg states). Moreover, rather than having nearly harmonic wells separated by high energy barriers—as usually found in the ground state—excited-state surfaces are often anharmonic, with multiple wells separated by low energy barriers, allowing the molecule to reach geometrical conformations far from chemical intuition.

The development of experimental femtosecond spectroscopic techniques [26, 27] has been a driving force pushing theoretical research in excited states beyond simple assignment of vertically excited spectra. The need for theoretical models helping to deconvolute time-dependent spectra has continually motivated the research of excited-state reaction pathways and excited-state dynamics.
In this context, internal conversion processes have been a main field of theoretical research in excited states. After photoexcitation, the molecule can reach regions of the configuration space where the Born–Oppenheimer approximation breaks down (see Fig. 2). In particular, degeneracy between states of the same spin multiplicity, also known as conical intersections [28, 29], creates an efficient funnel for radiationless transfer between adiabatic states. Seams of conical intersections are ubiquitous [30]; the main question to be answered is whether a specific molecule excited at a determined wavelength can reach the intersection seam or not.

Algorithms for localization of conical intersection have been developed [31–33], making their search comparable to the conventional search for stationary points. They are reviewed and benchmarked in Ref. [34]. The research of internal conversion pathways performed for a large variety of molecules has shown that the structures at conical intersections often keep close structural resemblance even between very different molecules. For instance, two examples of S1/S0 conical intersections are shown for two distinct molecules in Fig. 3. The substructure that causes the degeneracy between the two states is a twist-pyramidalized configuration (indicated by lines in bold) in both cases. The twist has the effect of stabilizing the pp* state and destabilizing the closed shell (cs) state, bringing them to an avoided crossing. Pyramidalization (sp2 to sp3 hybridization change) tunes the degeneracy [35]. Five of the most common motifs giving rise to S1/S0 conical intersections in organic molecules are collected and illustrated in Table 1.

In spite of the large variety of types of processes observed in molecular photodynamics, these motifs for conical intersections indicate that there are common patterns followed by molecules. For instance, Fig. 4 shows the state occupation during dynamics of pyrrole [38], adenine [39], and pyridone [40] according to surface hopping simulations. These state occupations belong to three distinct classes of excited-state pathways commonly observed in dynamics of organic molecules. For pyrrole, a very fast (sub-100 fs) dynamics occurs following the NH dissociation along the pr* state. For adenine, ring puckering toward an ethylenic conical intersection along the pp* state controls the dynamics. For pyridone, the conical intersection cannot be reached efficiently turning this molecule into a fluorescent species.

2.2 Charge transfer and excitonic interactions

If two or more chromophores interact with each other, new intriguing phenomena come into play. Strong interactions may significantly alter the character of the excited states by delocalizing them among several fragments. Additionally, defect migration plays a role even at much weaker coupling strengths and energy transfer occurs up to a spatial separation of several nanometers between chromophores [25]. Electronic defects in aggregated or bulk systems are commonly described in terms of excess electrons and holes relative to the neutral ground state. If the electron and the hole are in close contact, possibly delocalized over a few fragments, the term Frenkel exciton is commonly used. Typically, only Frenkel excitons are active in absorption and emission processes. Later, they may split into charge-transfer states, i.e., an electron and a hole on separate fragments bound by a strong mutual Coulomb interaction. Finally, complete charge separation can occur where the electron and hole migrate independently. The complete description of these phenomena is quite challenging as it is not only necessary to describe the electronic structure at
Table 1 Common motifs or “primitive conical intersections” giving rise to conical intersections between the first excited and the ground singlet states of organic molecules

<table>
<thead>
<tr>
<th>Conical intersection</th>
<th>Primitive structure</th>
<th>Examples</th>
</tr>
</thead>
<tbody>
<tr>
<td>Twisted;</td>
<td></td>
<td>Conjugated chains (ethylene [189], polar substituted ethylenes [190],</td>
</tr>
<tr>
<td>Twisted-pyramidalized</td>
<td></td>
<td>protonated Schiff bases [191], stilbene [192], azobenzene [193])</td>
</tr>
<tr>
<td>(pp*/cs)</td>
<td></td>
<td>Aromatic rings (benzene [194], purines [195], pyrimidines [196])</td>
</tr>
<tr>
<td>H-migration/carbene</td>
<td></td>
<td>Ethylidene [197]</td>
</tr>
<tr>
<td>(pp*/cs)</td>
<td></td>
<td>Cyclohexene [198]</td>
</tr>
<tr>
<td>Out-of-plane O (pO*/cs)</td>
<td></td>
<td>Formamide [199]</td>
</tr>
<tr>
<td>Bond breaking; ring</td>
<td></td>
<td>Rings with carbonyl groups (pyridone [40], pyrimidines [200], guanine</td>
</tr>
<tr>
<td>opening (prX*/cs)</td>
<td></td>
<td>[201])</td>
</tr>
<tr>
<td>Proton transfer (pp*/cs)</td>
<td></td>
<td>Heteroaromatic rings (pyrrole [202, 203], purines [204], thiophene [205],</td>
</tr>
<tr>
<td></td>
<td></td>
<td>furan [206], imidazole [207])</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Watson–Crick base pairs [118]</td>
</tr>
</tbody>
</table>

In Fig. 5 the model shape of a potential energy surface (PES) of a defect located on two interacting fragments is shown, cf. Ref. [41]. The diabatic states $H_{\text{diab}}$ and $H_{\text{diab}}$ where the defect is localized on the initial or fi fragments are represented by displaced parabolas. These are characterized by the reorganization energy $k$, the energy required to move from one minimum geometry to the other while staying on the same diabatic surface. These diabatic curves are modulated in this example by a constant coupling $H_{\text{diab}}$ to yield the adiabatic energy curves $E_{\text{ad}}$ and $E_{\text{ad}}$. If the two fragments are different, then a non-vanishing reaction free energy $D_{\text{r}}$ for the defect transfer reaction will be observed. If the coupling is on the order of the reorganization energy, then the resulting adiabatic states are strongly mixed and a unique delocalized minimum is formed, Fig. 5a. If the coupling is significantly smaller, then the adiabatic states remain very similar in character to that of the localized diabatic states and only at the transition region an interaction between the states occurs, Fig. 5b. The essence of Marcus theory is to combine $H_{\text{r}}$, $E_{\text{ad}}$, and $D_{\text{r}}$ to form a rate equation including non-adiabatic effects for weak coupling cases [42]. Förster theory allows connecting spectroscopically available quantities to form a rate equation of excitation energy transfer [43].
3 Quantum chemical method for excited states

3.1 Ab initio methods

Many ab initio methods are currently available for excited-state calculations. Some single-reference methods, such as the second-order approximate coupled-cluster (CC2) [44], algebraic diagrammatic construction (ADC) [45], and the equation-of-motion coupled-cluster (EOM-CC) [46] methods, have proven to be reliable and affordable sources for vertical excitation energy calculations, with data quality considerably superior to former common approximations such as the configuration interaction with single excitations (CIS) [47]. It should be noted that combination of CC2 and ADC(2) with the resolution-of-the-identity (RI) approximation [48, 49] has significantly increased the applicability of these methods (see below).

At strongly distorted molecular geometries or conical intersections with the ground state, the Hartree–Fock method does not provide a satisfactory reference wave function. In these cases, the usage of multiconfigurational and multireference methods is necessary, and the multiconfigurational self-consistent field (MCSCF) [50, 51], the multireference configuration interaction (MRCI) [52–54], or the complete active space perturbation theory to second-order (CASPT2) [55] can be applied. Analytical gradients are available for all these methods [56–58]. Analytical nonadiabatic couplings terms are available for MCSCF and MRCI methods [59].

Besides the high computational costs common to all these methods, another handicap affecting especially the MCSCF and the MRCI methods is their dependence on the choice of active and reference spaces [60]. Of particular concern is that larger active spaces, which are often used when a large number of orbitals is to be considered, start to include dynamic electron correlation effects for some of the electrons, which causes an imbalance by leaving the other electrons uncorrelated [61]. Additionally, convergence problems may increase computation times, and certain orbital rotations may appear for specific geometries changing the character of the MCSCF wavefunction that can lead to discontinuities in potential energy surfaces. MCSCF and MRCI often overestimate the energy of ionic states in the Franck–Condon region [62, 63]. CASPT2, on its turn, tends to underestimate the vertical spectrum [64, 65]. A collection of references to investigations benchmarking results for excited-state calculations at ab initio levels are given in Table 2.

3.2 DFT-based methods

Currently, excited-state properties can be obtained with several density functional (DFT) methods. Besides the popular time-dependent (TD) DFT [66, 67], usually computed within the linear-response approximation, other DFT-based methods, such as the restricted open-shell Kohn–Sham (ROKS) [68], restricted ensemble-reference Kohn–Sham (REKS) [69], time-dependent density functional tight-binding (TD-DFTB) [70], and DFT/MRCI [71, 72], can provide excitation energies and other properties. Among these methods, analytic energy gradients and analytic and numeric nonadiabatic couplings terms are available for TDDFT [73–78].

The result of a TDDFT calculation critically depends on the functional used. Because of its superior quality in ground-state calculations, the hybrid B3-LYP [79] functional is often used as a starting point. In a similar sense,
the generalized gradient approximation functional PBE [80] is often applied. PBE0 [81] is a parameter free hybrid extension of PBE, which was formulated with a special focus on molecular properties and excited states. Highly parameterized functionals like Truhlar’s M06 series [82] give remarkable results in many cases, but have the disadvantage that the physical understanding of the functional form becomes more difficult. In practical applications, usually several functionals would be considered and computed results compared to reference values (obtained, e.g., from experiment or a high-level ab initio method) thus allowing to find an appropriate functional. A difficulty for applying TDDFT is the large number of available functionals, from which it is not trivial to find the best one for each specific case. Additionally, TDDFT lacks the possibility of systematically improving results, which is one of the major characteristics of ab initio methods.

One of the main problems with DFT-based methods has been the description of charge-transfer states [83], which can be strongly overstabilized by conventional functionals. This problem, however, has been largely attenuated by the development of asymptotically corrected functionals [82, 84, 85], but more experience may still be needed to properly evaluate these approaches. In the case of TDDFT, the single-reference character and the linear-response approximation also turn the computation of potential energy surfaces near conical intersections between the ground and the excited states problematic, if not impossible. These intersections can be described by ROKS (within a simple two-state approximation), REKS, and DFT/MRCI methods.

A collection of references to works benchmarking results for excited-state calculations at DFT-based levels are given in Table 2.

3.3 Semiempirical-based methods

As for ground-state problems, one promising option to overcome the limitations imposed by computational costs is the use of semiempirical methods. Semiempirical-based methods have been also developed for excited-state calculations. In particular, multireference problems have received special attention with the development of semiempirical configuration interaction methods employing floating-occupation of molecular orbitals (FOMO/CI) [86] and MRCI based on the graphic unitary group approach (GUGA) [87].

Results of mixed quality have been reported from the application of these methods. Good results, for instance, can be obtained for vertical excitations with the OM2/MRCI method [88]. The excited-state relaxation dynamics, however, has been often in contradiction with results obtained at ab initio levels (see, for instance, the discussion about cytosine in Sect. 6.1). Transferable, large-scale parametrization over the whole periodic table and including excited-state stationary structures and intersections is still necessary to make these methods fully reliable for excited-state calculations.

4 Methods for photodynamical simulations

4.1 Wavepacket dynamics

The full time-dependent Schrödinger equation for a molecule can be partitioned between self-consistent sets of equations for the electronic and nuclear systems [28, 89]. Then, the nuclear wavepacket of an electronically excited molecule can be propagated by grid-projection techniques [90, 91]. The problem with such methods is that only a limited small number of nuclear coordinates can be included in the calculations. Even though the situation is improved by time-dependent wavefunction expansions, like in the multiconfigurational time-dependent Hartree (MCTDH) method [89], computational costs and difficulties involved in building multidimensional potential energy and coupling surfaces still limit wavepacket propagation to small subsets of nuclear coordinates.

In spite of such limitations, excited-state wavepacket dynamics is an important tool for obtaining highly accurate spectroscopic results [89, 92] or verifying the quality of predictions obtained with trajectory-based methods [93, 94].

4.2 Trajectory-based approaches

Trajectory-based approaches for nonadiabatic dynamics simulations have been popularized in the last decade. They overcome the main problem of nuclear wavepacket propagation—the limited dimensionality due to computational costs and to difficulties of building multidimensional potential energy surfaces—by adopting a local approximation. Within the local approximation, energies, energy gradients, and coupling terms need to be computed only along a classical trajectory, rather than over the full space as the time-dependent Schrödinger equation requests. Delocalization of the nuclear wavepacket is partially recovered by the propagation of multiple independent trajectories. Nonadiabatic behavior is recovered by different approaches. Two of the most well-tested trajectory-based methods are multiple spawning [13, 95] and surface hopping [96].

While multiple spawning propagates Gaussian wavepackets centered at classical trajectories and can spawn new trajectories at nonadiabatic crossing regions, surface hopping propagates classical trajectories on the energy surface of a single state, allowing each independent
trajectory to switch between states during the propagation according to a stochastic algorithm. The multiple spawning technique has the advantage of including quantum effects for the nuclear motion more rigorously. Surface hopping is widely used because of its methodological simplicity and ease of interpretation. In many cases, multiple spawning and surface hopping should lead to similar results at similar computational costs if a proper integration of the time-dependent Schrödinger equation and some additional consistency corrections [97] are performed in the surface hopping dynamics. A recent review about the multiple spawning method can be found in Ref. [98]. Surface hopping dynamics has been reviewed in Refs. [99, 100] and a general program implementation is described in Ref. [101].

5 Computational considerations for dimers and aggregates

A significant amount of attention has been devoted to computing the electronic coupling between chromophores as the central descriptive quantity for the defect transfer process, cf. Fig. 5. There are two general approaches for computing these couplings: direct supermolecular computations and computations of interaction matrix elements between molecules considered independently. In the supermolecular approach, the coupling is obtained as half the energy splitting at resonance conditions [102]. Resonance can either be enforced by symmetry considerations, cf. Refs. [103, 104], by scanning of geometries, or by applying an external electric field [105]. It has been pointed out that simply calculating the gap without checking for resonance may significantly overestimate the coupling [103]. Alternatively, localized states in supermolecular structures may be found by property-based diabatization schemes [102, 105]. In a third approach, the parameters are obtained by considering repeating units [106]. If the two chromophores are considered separately, the task is to compute the interaction matrix element between the two excited states. If there is no overlap between donor and acceptor wave functions, exchange can be neglected and the coupling is given as the Coulomb interaction between the transition densities [107]. This electrostatic interaction can be computed according to the transition density cube method [108] or using analytical Coulomb integrals [107]. For larger separations between the chromophores it is often enough to consider the interaction of transition dipoles, which is the basis for Förster theory. If charge migration rather than energy migration properties are to be computed in a fragment-based approach, the coupling can be estimated as the matrix element between the highest occupied molecular orbitals of the fragments [103, 109]. If the couplings and other descriptive quantities are available, they can provide the background for global theories or multi-scale techniques to describe larger systems [22, 41, 110, 111].

In many cases, it is advantageous to go beyond the simple rate equations provided by Marcus and Förster theory. This was done by adapting the existing theories through inclusion of vibronic terms [41] or by explicitly considering molecular aggregates [111]. But atomistic ab initio non-adiabatic dynamics simulations, as described above, should give a direct unbiased view of the processes occurring and can naturally be applied to intermediate coupling situations where Marcus and Förster theory cannot be applied. An examination of the applicability of surface hopping dynamics for defect transport and its connection to Marcus theory is given in Ref. [104]; the underlying physics are outlined in Sect. 2 of Ref. [112]. The atomistic picture allows for an inclusion of environmental effects through QM/MM coupling schemes. In particular, electrostatic embedding (see Ref. [113] and further references therein) allows coupling the electronic polarization of the core system directly to the orientational polarization of the solvent. The strong influence of such an environmental polarization on the charge-transfer properties of DNA have been discussed in Ref. [109].

6 Applications showing current possibilities and future aspects

6.1 Nucleobases

A very active field of theoretical research in excited states has been the investigation of the behavior of nucleobases [1, 114, 115] and other nucleic-acids fragments [116–118] after UV irradiation. The main motivation has been to understand how this radiation can damage the genetic code and what intrinsic protection mechanisms DNA has developed against it. Experimental research has revealed that all nucleobases can efficiently get rid of the photoenergy at the picosecond time scale [119, 120]. Theoretical research of reaction pathways and conical intersections of nucleobases has identified the main internal conversion channels available for each nucleobase [1, 121–124]. Dynamics simulations have provided information about the efficiency of each of those reaction pathways [20, 114, 115, 125, 126].

Although the reaction pathways described by most of theoretical methods are qualitatively equivalent, results of the dynamics simulations can be quite dependent on the specific properties of the respective potential energy surfaces. Divergent results about the importance of each pathway have been found for all nucleobases. This situation is illustrated for cytosine in Table 3, which surveys the results of simulations from Refs. [114, 115, 117, 126–129].
Table 3  Gas phase dynamics results for UV-excited cytosine obtained with different methods

<table>
<thead>
<tr>
<th>Dynamics</th>
<th>Electronic structure</th>
<th>Main pathway</th>
<th>s (ps)</th>
<th>Refs.</th>
</tr>
</thead>
<tbody>
<tr>
<td>MS</td>
<td>CAS (2, 2)</td>
<td>oop-NH₂ (65%)</td>
<td>0.8</td>
<td>[127]</td>
</tr>
<tr>
<td>SH</td>
<td>OM2/MRCI</td>
<td>C6-puck (100%)</td>
<td>0.37</td>
<td>[115]</td>
</tr>
<tr>
<td>SH</td>
<td>CAS (10, 8)</td>
<td>Quasi-planar (64%)</td>
<td>0.69</td>
<td>[114, 128]</td>
</tr>
<tr>
<td>SH</td>
<td>CAS (12, 9)</td>
<td>Quasi-planar</td>
<td>0.5²</td>
<td>[129]</td>
</tr>
<tr>
<td>SH</td>
<td>FOMO/AM1 (PM3)</td>
<td>C6-puck (77%)b</td>
<td>0.09 (0.17)</td>
<td>[117]</td>
</tr>
<tr>
<td>SH</td>
<td>ROKS</td>
<td>C6-puck</td>
<td>0.7</td>
<td>[126]</td>
</tr>
</tbody>
</table>

MS multiple spawning, SH surface hopping

* Extrapolation of the reported data with a single exponential fitting function

b Cytosine sugar

c Isolated cytosine

It is well established that cytosine has three main reaction pathways for internal conversion after excitation into the first bright pp* singlet state [1, 124, 127]. One pathway is characterized by puckering at the C6 atom, another one is characterized by out-of-plane displacement of the amino group, and the third one is characterized by a quasi-planar distortion bringing cytosine to a near three-state conical intersection. As shown in Table 3, although all methods predict ultrafast deactivation, there is still no consensus about which pathway is the most important one.

Semi-classical simulations of the UV-photo absorption spectrum at the RI-CC2 level were carried out for each nucleobase, adenine, guanine, cytosine, thymine, and uracil in gas phase [18]. The simulation of the absorption cross section was approached by constructing a nuclear phase space distribution in the electronic ground state and then projecting it onto the electronic excited states. The ground-state distribution was prepared by means of a probabilistic sampling of the Wigner distribution for the ground-state quantum harmonic oscillator [32, 130, 131]. The spectra of adenine, guanine, thymine, and uracil (Fig. 6) showed a common characteristic by the presence of a two-band structure separated by a low intensity region. On the other hand, the cytosine spectrum is formed by a succession of three bands of increasing intensity (Fig. 6). For all five nucleobases, the bands are formed mostly by absorption into pp* states.

6.2 DNA fragments

Whereas most of the photophysics of isolated nucleobases is now quite well understood, the photodynamics of several interacting nucleobases still poses many challenges. Research on the excitonic interactions between nucleobases is driven by the observation that the photophysics of DNA is significantly different from that of isolated nucleobases. Whereas all the isolated bases decay on a picosecond time scale [119, 120], long-lived transients up to 10–100 ps [132–134] are observed in DNA, which are strongly dependent on sequence and structure [135]. In principle, both inter- and intrastrand interactions could play a significant role. It is now believed that intrastrand stacking interactions are the major factor for the increase in lifetime [2]. It has been suggested that UV absorption occurs into Frenkel excitonic states with a delocalization length of 3–4 bases in a homo-adenine strand [134] or probably less in more heterogenous sequences [2].

Computational studies on DNA base stacks are aimed at elucidating the processes described above. Computational challenges arise from the large system sizes to be treated, the importance of the environment, and the need of considering dynamical effects. In principle, TDDFT would be favorable for describing systems of such a size and base tetramers have been successfully treated [136], but the accuracy of TDDFT, at least in the case of standard functionals without long-range corrections, has been questioned [137]. Ab initio methods have been used for
slightly smaller systems. RI-CC2 has been used for system sizes up to base trimers [106], and the CASPT2 method could be applied to dimers [138]. It is a particular challenge to assess the involvement of charge-transfer states. TDDFT studies using a polarized continuum model emphasized the importance of charge-transfer states even when long-range corrected functionals were used [139, 140]. By contrast, a CASPT2 study concluded that Frenkel excitonic states stabilized by resonant interactions should be the most stable trapping sites [138]. Clarifications are still needed to understand these essential photophysical processes. More information may be provided by ab initio methods combined with QM/MM electrostatic embedding treatment of the surrounding DNA to treat both the electronic structure and the polarization of the environment at a high level.

Extended benchmark calculations for excitation energies, oscillator strengths, and characters of the low-lying singlet excited states of the stacked nucleobase pairs adenine–thymine (AT) and guanine–cytosine (GC) were performed by means of a selected set of density functional, B3-LYP and PBE0, and the recently developed M06-2X and M06-HF within the time-dependent density functional theory (TD-DFT) [141]. The resolution-of-the-identity second-order algebraic diagrammatic construction (RI-ADC(2)) method served as reference approach for comparison. For the AT dimer at its ground-state optimized geometry, the charge-transfer state at RI-ADC(2)/TZVP level corresponds to the excited state S_\alpha, which is an excitation from a \( p \) orbital in adenine to a \( p^* \) in thymine. For the GC dimer, the RI-ADC(2)/TZVP the charge-transfer state corresponds to S_\alpha, which is a \( p-p^* \) excitation from guanine to cytosine. Comparison of DFT and ADC(2) methods shows that the M06-2X version provides a relatively good reproduction of the reference results. It avoids the serious overestimation and overcrowding of the spectrum with charge-transfer states found with the B3LYP functional. Solvent effect was also investigated for the AT and GC complexes. The main observation is that the amount of charge-transfer character increases with the polarity of the solvent.

Non-adiabatic dynamics simulations have been performed for one quantum mechanically treated base in an MM base stack [142] and a short double helix [143]. The study illustrated that purely mechanical restrictions do not play a large role and that the monomer likely decay pathways are not hindered by the stacking interaction.

Interactions between Watson–Crick base pairs in DNA could lead to electron or proton transfer processes between the strands as well. The possibility of an electron-driven proton transfer in a guanine-cytosine base pair has been suggested from a static computational study [118] and further examined by dynamics simulations [116]. The effect has been found experimentally in isolated base pairs [144]. But it is now believed that interstrand interactions do not play a significant role in the photophysics of DNA strands [2, 136].

A significant amount of attention has been devoted to charge migration dynamics of DNA [21, 109, 145]. Also in this case, the question of delocalization and of transport properties arises. Aside from biological interests, charge transfer in DNA has been studied in the context of nanotechnology as a model self-assembling system with molecular recognition properties. The task in this context is to modify the properties in order to get sufficient electric conductivity [21]. It has been theoretically suggested [146] and experimentally verified [145] that charge transfer may proceed through two distinct mechanisms: direct superexchange up to a separation of about three bases and multistep hopping for larger distances. Several strategies exist for getting a detailed picture of different aspects of these processes. Models from solid state physics are able to capture the periodicity of the system but have difficulties in properly considering structural fluctuations and molecular motions [21, 147]. High-level ab initio supermolecular calculations (CASSCF, CASPT2, and MRCI) give detailed descriptions of the interactions between stacked bases [148, 149] and even non-adiabatic effects in connection with dynamics simulations, cf. Ref. [104]. However, these methods can only be applied selectively because of high computational requirements. In contrast, semiempirical DFTB calculations in connection with QM/MM inclusion of the environment allow for an efficient sampling of the conformational space and for estimating the importance of solvent degrees of freedom [109].

6.3 Retinal and model systems

Retinal, the chromophore of rhodopsins, has attracted attention from theoreticians since the 1970s [150]. It plays a main function in the transduction of a light signal into a chemical impulse via photoisomerization inside the protein cage. Theoretical research of retinal has been focused on two main aspects, first, solvatochromic effects, which allow its absorption to be tuned to different wavelengths depending on the protein-specific environment [151–154]; second, determination of isomerization mechanism occurring after photoexcitation [4, 5, 155]. Along the last decade, most of the investigations in this field dealt with retinal models [156–161], usually protonated Schiff bases neglecting the cyclohexene ring. Recently, research considering the full length retinal at quantum mechanical level has been reported [4, 5, 155].

The photoisomerization mechanism is still an issue under debate. While ab initio (CASSCF, CASPT2, MRCI) [155–157] and semiempirical (OM2/MRCI) [159] methods predict that torsion around formal double bonds is the main mechanism bringing the molecule to the conical intersection, TDDFT results predict a different scenario with a
major role played by torsion around formal single bonds [162]. Although the agreement about the torsional mode coming from most of methods seems to indicate a failure of TDDFT to deal with this molecule, recent CASPT2 and quantum Monte Carlo evaluations of excited-state potential energy surfaces of a retinal model indicated that the changes in bond length alternation in the excited state should be much smaller than that predicted by CASSCF and even MRCI, which would favor to some extent the TDDFT predictions [163].

6.4 Photovoltaics

Electronic devices based on organic chemistry have many potential advantageous properties compared to silicon-based devices. These include lower production costs, ease of processing, and mechanical flexibility [24]. In particular, the field of photovoltaics has been intensively studied with the aim of producing photovoltaic energy at a comparable or lower cost as traditional non-renewable energy sources. Computational studies are aimed at elucidating the complex nature of the excited states involved and to examine the vibronic coupling that leads to interconversion between them, partially on an ultrafast time scale. A variety of interesting classes of solar cells have been suggested. In dye-sensitized solar cells, an organic dye is used as a chromophore in direct contact with an inorganic framework and charge separation occurs at the interface between the dye molecules and inorganic nanoparticles [164, 165]. If an organic bulk phase is to be used, then the exciton migration properties play a decisive role. The poly (p-phenylene vinylene) (PPV) system and its methoxy derivative have been extensively studied in this context. A special focus was laid on coherences in energy migration [166], which were explained in terms of excitons surfing on the polymer backbone [167]. A DFT study illustrated the strong electron–phonon coupling along the bond length alternation coordinates [168], which could serve as a basis for the surfing process. Whereas bond length alternation is expected to affect on-site excitation energies, torsions may modulate the electronic couplings between the different monomer units. Using full quantum dynamics, these nuclear coordinates can be coupled with electronic degrees of freedom and valuable information about electron–phonon coupling and possible quantum coherences could be obtained, cf. the preliminary exploration of Ref. [110].

After exciton migration, charge separation has to occur at the heterojunction. This process is not well understood yet [12], but quantum dynamical studies may give insight into the electron–phonon coupling processes involved. After charge separation, the charge migration properties become the decisive feature. Computational studies on charge transport in organic systems have been concerned with the estimation of transfer parameters [103] as well as with non-adiabatic dynamics simulations [169]. A number of interesting extensions exists for making organic solar cells more efficient. Self-assembled nanoscale heterojunctions may be used for decreasing exciton migration lengths [170]. Alternatively, supramolecular assemblies with an electron donating group, a chromophore, and an electron accepting group covalently connected can eliminate the need of diffuse electron migration altogether. The properties of such a triad have been studied by DFT [171] and TDDFT [172]. Moreover, the process of multiple exciton generation from one photon can be used to increase the fundamental limits of conversion efficiency [173]. In organic molecules, this can be realized through singlet fission, i.e., one singlet exciton is split into two triplet excitons [173]. The process has been examined computationally for a pentacene dimer [174]. It is suggested that the photoexcitation occurs into a bright single excitation $S_2$ state, which can cross with a dark doubly excited lower lying state. After this state is reached the two molecules repel each other, and as the system dissociates the doubly excited state obtains the nature of two singlet coupled triplets [174, 175]. To describe these complex excited states, multi-reference perturbation theory was applied with a triple zeta basis set [174]. Biomimetic solar cells using porphyrin aggregates are another promising strategy [176]. In this case, a connection between large-scale theories [22] and smaller-scale parameter calculations may be suitable to provide a solid theoretical background. In general, it can be said that computational studies provide a foundation for understanding the signatures of complex excited-state processes, and may therefore aid in the design of new efficient solar cells in the different categories described.

6.5 Photodevices, phototriggers, and molecular machines

In analogy to the processes occurring in nature for retinal (see Sect. 6.3), molecular photodevices can be used for a clean and ultrafast way to control reactions and trigger processes [177]. Theoretical research in this field has been focusing on laser control of reactions, such as to induce photoisomerization [15, 178, 179], photodissociation [9, 180], and proton transfer processes [181–184]. Light-driven motors have been considered as well [185].

One of the main examples in this field is the photoisomerization of azo-molecules, especially of azobenzene [15, 178, 186, 187], whose molecular length is strongly affected by photoexcitation. In fact, theoretical investigations have played a major role in this field by means of dynamics simulations, which have revealed the intrinsically multidimensional character of the photoisomerization process, rather than a simple unidimensional one, as commonly thought.
Photoexcitation may induce electron or proton transfer within the molecule or between molecules. This process leads to a strong red shift of the emission wavelength in comparison with the absorption wavelength. Theoretical studies of excited-state intramolecular proton transfer (ESIPT) have been useful to support experimental ultrafast spectroscopic investigations. These studies have revealed, for instance, details on the transfer mechanism [181–183] and how it may trigger internal conversion processes [36, 188]. Another interesting theoretical suggestion was a reversible molecular switch based on ESIPT [184].

7 Conclusion and outlook

After photoexcitation, molecules may undergo a variety of different processes. The excited states are characterized by a significant shift in electron density, which may, for example, lead to ionic or diffuse character. In addition, excited states can interact, resulting in irregular shapes of potential energy surfaces. Ultrafast non-equilibrium processes further complicate the situation. For these reasons, excited-state calculations are still quite challenging in spite of the large effort spent in developing new computational methods. Whereas ground-state thermochemistry has evolved into a field where many questions can be routinely addressed by non-specialists, excited-state calculations usually still require a careful assessment of available methods. Not only considerations of computational efficiency play a role, but methods have to be chosen that are appropriate to describe the different kinds of excited states and processes of interest. The availability of analytic energy gradients and nonadiabatic coupling elements is also an important selection criterion.

A major goal in the development of new excited-state methods will be the increase of applicability and stability of the different approaches. Many coupled-cluster-based single-reference methods exist, which offer high-quality results at geometries close to the ground-state minimum. However, the description of conical intersections and strongly distorted geometries is still highly challenging. It would be highly desirable to have a unified approach for these multi-reference cases, rather than having to carefully choose the methodological details as is currently the case for many such problems. TDDFT serves as an attractive method because of its computational efficiency, but it suffers from different systematic errors, most prominently the overstabilization of charge-transfer states. Long-range corrected functionals offer a promising solution. Semiempirical methods offer an even computationally faster approach and appropriate multireference methods are available, but careful parameterization is usually necessary and questions about transferability arise. When choosing a dynamics method, it is necessary to compromise between computational efficiency and the level of approximation, i.e., whether nonadiabatic effects and all internal degrees of freedom have to be considered or not. Dimers and aggregates offer new challenges that may have to be addressed with efficient multi-scale methodology. While there are many successful applications of present methods, there are still many outstanding problems remaining and the development of new approaches to electronic structure calculations will play an important role.

Acknowledgments This work has been supported by the Austrian Science Fund within the framework of the Special Research Program F41 Vienna Computational Materials Laboratory (ViCoM). FP is a recipient of a DOC fellowship of the Austrian Academy of Sciences. The calculations were performed in part at the Vienna Scientific Cluster (project nos. 70019 and 70151) of the Vienna University Computer Centre. This work was also performed as part of research supported by the National Science Foundation Partnership in International Research and Education (PIRE) Grant No. OISE-0730114; support was also provided by the Robert A. Welch Foundation under Grant No. D-0005.

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