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Theoretical Methods of Investigation of Excited States of Organic Molecules

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Abstarct–A brief review of quantum-chemical methods applied to describe excited states of organic molecules is presented. The main emphasis is put on advantages and disadvantages of widely used computational techniques. A brief summary of the performance of such methods and practical recommendations on their use is included.

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Correct prediction of the energies of excited states of molecules and of the probabilities of electron transitions is, along with calculation of potential energy surfaces, necessary for explanation and interpretation of the electronic spectra of molecular systems. The intricate nature of this task is associated with the necessity to account both for dynamic electron correlation that dominates in closed-shell molecular systems and for nondynamic correlation that plays a key role in quasidegenerate electron states characteristic of most excited states. Therefore, whether one or another theoretical approach allows one to include completely correlation effects largely determines the applicability of this approach for investigating excited states of molecular systems. Furthermore, the calculation method should provide a real picture of molecular excited states whose wave functions should be mutually orthogonal, which is prerequisite for calculating properties of electron transitions. If the space and spin symmetries of an excited state in focus are the same as those of a lower lying state, the method should not allow variational collapse of the former state. This condition is especially for dynamic studies of excited states, since geometry relaxation of molecular systems is often associated with their symmetry reduction.

The present review is devoted to quantum-chemical methods for investigating excited states and their practical performance in predicting the energies of the excited states involved in optical transitions in organic systems (for a more detailed consideration of the theoretical principles and applications of such methods, see, for example, reviews [1, 2]). Here we focus largely on the widest used methods incorporated in most quantum-chemical programs.

In cases where the single-determinant approximation is sufficiently coorrect for both the ground and excited states of molecules, lowest energy states differing by multiplicity or (and) related to different irreducible representations of symmetry point groups can be calculated. The calculation reduces to the solution of an SCF equation by the spin-unrestricted Hartree–Fock (HF) method. The excitation energy is calculated in this case as the difference of the energies of the ground and excited states obtained in two independent calculations. As known, the disadvantage of this approach is the loss of the spin frequency of the wave function. Consequently, the solution is no longer an eigenvalue of the squared full spin operator, which results in inadequate assessment of molecular properties. Furthermore, this approach is fully unsuitable for calculating higher excited state of a given symmetry.

A more universal approach to excited state calculations is the configuration interaction (CI) method [3–6]. Generally, the CI approximation is based on the expansion of the ground state wave function in the excited determinants formed by swapping one or several occupied by virtual orbitals in the Stater determinant which is a solution of the ground state HF equation:

$$\Psi_{\mathrm{CI}} = \Psi_0 + \sum_{i,a} C_i^a \Psi_i^a + \sum_{ijab} C_{ij}^{ab} \Psi_{ij}^{ab} + \ldots \qquad (1)$$

where Ψ_0 is the ground state HF determinant; the $i, j, \ldots$ indices relate to occupied orbitals and $a, b, \ldots$, to virtual.

Provided all possible excited states are included, expansion (1) gives an exact solution of the HF equations for a given basis. This method was given the name the full congiguration interaction (FCI) method. This method, in view of huge computational expenses, is feasible only for small molecular systems, and, therefore, truncated versions of expansion (1), such as CIS, CISD, and CISDT, are used. Let us dwell initially on the most widespread CI method which deals exclusively with single excitations (CIS) [4]. In this approximation, Eq. (1) contains only two first terms. The calculation of the transition energies and wave functions of excited states reduced to solution of eigenvalue equations written in matrix notation as

$$\mathbf{AX} = \omega \mathbf{X}, \qquad (2)$$

where **A** is the matrix whose elements contain differences of orbital energies ε and antisymmetrized two-electron integrals:

$$A_{ia,jb} = (\varepsilon_a - \varepsilon_i)\delta_{ij}\delta_{ab} + (ia\|jb), \qquad (3)$$

$$(ia\|jb) = \iint dr dr' \frac{\varphi_i(r)\varphi_a(r)\varphi_j(r')\varphi_b(r') - \varphi_i(r)\varphi_j(r)\varphi_a(r')\varphi_b(r')}{|r - r'|}, \qquad (4)$$

X, matrix of the configuration expansion coefficients; and ω, diagonal matrix of the excitation energies. The roots of the corresponding secular equation

$$(A - \omega)\mathbf{X} = 0. \qquad (5)$$

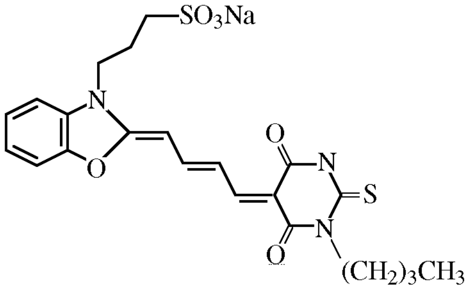
give the excitation energies, and its coefficients determine the wave function of the excited state. The excitation energies obtained by the variational procedure correspond to the upper limit of true values, and the corresponding wave functions are mutually orthogonal. For closed-shell molecular systems the CIS method provides spin-pure states.

In general, the CIS excitation energies are overestimated compared to experimental values. There are two main reasons for such a departure. First, the HF virtual energies of singly excited states (singles), which the excited state determinants are derived from, are calculated for an $(N + 1)$-electron system.

As a consequence, the orbital energy difference which determines the values of the matrix elements in Eq. (3), is a high ovestimatation for the excitation energy. Thus, the canonical orbitals are not a good basis for the expansion of the correlated wave function which should be highly flexible to compensate for this disadvantage. corresponding to higher level excited states. Second, the CIS method completely neglects dynamic electron correlation effects, the related errors in the excitation energy should compare with the electron pair correlation energy (~1 eV). Moreover, the contribution of correlation effects varies with electron state.

As an example, we can mention here the CIS/6-31+G* calculation of the first three singlet states of benzene: $^1B_{2u}$, $^1B_{1u}$, and $^1E_{1u}$ [7]. The calculated excitation energies are overestimated by 1.25, 0.11, and 0.8 eV, respectively, compared to experiment. The departure of the energies of the vertical (i.e. involving no structural changes) quantum transitions, obtained by CIS/6-31+G* calculations for pyridine, is of the same order [4]. In the latter case, the excitation energies for the first three singlet states $^1B_1$, $^1B_2$, and $^1A_2$ are higher than experimental values by 1.65, 1.31, and 1.97 eV.

Even though the CIS method results in highly overestimated excitation energies, it is still used, but the resulting values are subjected to linear scaling [8–10]. For example, Mach et al. [10] made use of the CIS/6-31+G* and CIS/6-311+G** methods to calculated the absorption spectra of Merocyanine 540 (**I**) and its phototransformation products:



I

Naturally, this method is applicable only when correlation effects contribute almost equal to all the excited states of interest.

The CIS results can be appreciably improved by introducing a correction for dynamic correlation, which is calculated by the second-order perturbation theory method which approximately accounts for double excitations. This method, CIS(D) [5, 6], as well as its version including spin component scaling (SCS) on the basis of the Møller–Plesset second-order perturbation theory (MP2)–SCS-CIS(D) [11] with the aug-cc-pVTZ basis set, were applied to calculate 0–0 transition energies for a series of organic molecules [12]. The mean average deviations of the theoretically predicted transition energies from experiment were 0,19 and 0,22 eV for CIS(D) and SCS-CIS(D), respectively. At the same time, the transition energies for the for the $^1B_{2u}$, $^1B_{1u,}$ and $^1E_{1u}$ excited states of benzene proved overestimated compared to observation by 0.43, 0.38, and 0.5 eV, respectively [CIS(D)]. Errors of the same order are involved in the calculated energies of the ^1L_a and ^1L_b states (Platt nomenclature [13]) of indole. Moreover, the deviations of calculation from experiment for different states of the same molecule may vary over a wide range. For example, the calculated transition energy for the ^1L_a excited state of styrene fits experiment very closely, whereas the respective value for the ^1L_b state is overestimated by 0.51 eV [CIS(D)] and 0,37 eV [SCS-CIS(D)]. This result is quite understandable: The contribution of electron correlation is generally dependent on the molecular state, but the correction to the excitation energy, introduced in the CIS(D) method, does not account for this dependence.

Another approach to excited state calculations is based on the coupled-cluster (CC) formalism [14–18]. This method is presently provides the most exact description of the ground-state properties of molecular systems, including more than 90% of dynamic correlation effects.

In the one-determinant CC version, the exact ground state function results from the action of an exponential cluster operator on a certain reference state:

$$| \Psi_{cc} \langle = e^{\hat{T}} | \Psi_0 \langle . \tag{6}$$

where $|\Psi_0>$ is the reference (commonly Hartree–Fock) determinant; $\check{T}$, cluster operator

$$\hat{T} = \sum_{\mu} t_{\mu} \hat{\tau}_{\mu}. \tag{7}$$

$$\hat{\tau}_{\mu} = \hat{\tau}_{ijk...}^{abc...} = a_a^+ a_b^+ a_j a_c^+ a_k \ ... \tag{8}$$

in which the a, b, c,... (i, j, k,...) indices relate to occupied (unoccupied) orbitals $|\Psi_0>$; t_μ, cluster amplitudes; and $a^+(a)$, creation (annihilation) electron operator.

The ground state energy energy and cluster amplitudes are determined from the Schrödinger equation:

$$e^{-\hat{T}} \hat{H} e^{\hat{T}} | \Psi_0 \langle = E | \Psi_0 \langle . \tag{9}$$

by projecting on the states $|\Psi_0>$ and $t_\mu|\Psi_0>$

$$\langle \Psi_0 | e^{-\hat{T}} \hat{H} e^{\hat{T}} | \Psi_0 \langle = E, \tag{10}$$

$$\langle \Psi_0 | \hat{\tau}_{\mu}^{+} e^{-\hat{T}} \hat{H} e^{\hat{T}} | \Psi_0 \langle = 0. \tag{11}$$

Since the $e^{-\check{T}}\hat{H}e^{\check{T}}$ operator is non-Hermitian, its eigenvalues are mutually nonorthogonal and, in the general case, can be linearly related to each other. The list of disadvantages can also be completed by the poor divergence of calculation results for excited states [19]. This gives rise to fundamental difficulties in attempted calculation of individual excited states for estimating the energies of quantum transitions.

In this connection, alternative approaches are used: the equation-of-motion coupled-cluster (EOM-CC) [20–28] and linear response coupled-cluster (LR-CC) methods in various approximations [29–32], and well as symmetry-adapted cluster configuration interaction (SAC-CI) method [33, 34].

In all standard CC methods, expansion (7) is truncated to the first three terms. An example is provided by an approximation that includes only singly and doubly excited states (CCSD) [35–37], as well as its popular version CCSD(T) [38] in which the dominative effect of triply excited clusters (triples) is included perturbatively in the CCSD energy.

The choice of a one-determinant ground-state wave function as zero approximation is a standard approach in coupled-cluster methods. Therefore, for sufficiently exact excitation energies higher order transitions should be included the expansion. Thus, for correct description of singly excited states one should include doubly excited states, and for the latter, triply excited.

This compensates, to a certain extent, for the disadvantages of the reference wave function and allows one to account for the multiconfigurational nature of excited states. In cases where the one-determinant approximation is sufficiently correct, coupled-cluster methods are the most exact calculation methods. If this condition is not met, the calculated excitation energies may essentially depart from experimental.

A characteristic example is provided by the calculations of the absorption spectra of the N_2 and C_2 molecules [39] whose ground states are multiconfigurational. The calculations showed that the wave functions of these states are much contributed by triply excited states and negligibly contributed by quadruple excitations. On the other hand, these molecules have a set of excited states of different nature. Some of them are preferentially singles and others are mostly contributed by doubles. Together the above two circumstances result in that the transition energy of the ^1D_g (doubly excited) state of C_2, calculated by the EOM–CCSD method depart from that calculated by the FCI method by 2.05 eV. This difference is of the same order as the transition energy in itself (2.293 eV). Even with the EOM-CCSDT method which includes triple excitations reduces the gap by as little as 0.4 eV. Coupled-cluster methods are insufficiently correct in the case of open-shell systems.

The limitations of the one-determinant approximation can be overcome in terms of the multi-configurational approach. Known versions of such methods, based on the coupled-cluster formalism [40–42], are computationally much more burdening than standard CC methods, but the latter are extremely laborious. Therefore, from the practical viewpoint, CC methods cannot compete with multiconfigurational methods based on the configuration interaction theory (MR–CI) [43–47]. Of them the most popular is the complete active space self-consistent field (CASSCF) method [46] and its version complete active space with second-order perturbation theory method (CASPT2) [47].

In the CASSCF theory, excited state configurations are distributed between orbital subspaces. The first, inactive subspace is formed by orbitals doubly occupied in all configurations; the following, secondary subspace is formed by orbitals unoccupied in all configurations; and the third, active space includes orbitals that can be filled in all possible ways. In a certain sense, we consider full configuration interaction is a restricted but variationally optimized space of active orbitals. Thus close-to-degenerate energy states of molecules are taken into account.

The CASPT2 method makes use of the CASSCF wave function as zero approximation, which includes a correction for dynamic correlation effects, which is calculated from perturbation theory and gives first-order corrections to the wave function and second-order corrections to the excitation energy. Thus, CASPT2 adequately includes both static and dynamic electron correlation.

In the CASPT2 method, the initial division of occupied orbitals into active and inactive is determined by a space of configurations in which electrons are distributed over active orbitals in all way possible in a given spatial and spin symmetry. If one or several orbitals essential for describing an electronic spectum are not included in the active space, the problem of so-called intruder states arises.

A characteristic example of such states is provided by diffuse states. The contribution of dynamic correlation effects in this case is smaller than in the case of the more compact core excited states. As a result, at a zero approximation level, diffuse states prove to be artefactually stabilized with respect to core states. This can lead to situations when the electronic states of a molecule turn to be accidentally degenerate. The simplest way to go around these problems is to extend the active space. However, the size of active space is restricted by the technical potential of modern computational techniques, which allows no more than 12–14 active orbitals to be considered. Therefore, another approach this task is used, based on the introduction into the zero approximation Hamiltonian of a small shift of levels [48].

Due to the balanced inclusion of dynamic and static electron correlation effects, the CASPT2 method allows sufficiently accurate (~0,2 eV) calculations of excited state energies [49–54]. However, if the CASSCF wave function is an insufficiently good approximation, large calculation errors may arise. An example is provided by the results of Serrano–Andres et al. [55] for the electronic spectra of imidazole whose core excited states A' are strongly mixed with low-lying Ridberg states [56]. In this case, the absolute difference in the calculated and experimental gas-phase transition energies is, on average, 0.3 eV.

While offering a number of undeniable advantages, CASPT2 still works well only with medium-sized molecular systems (~20 atoms). Furthermore, the right choice of active space, which eventually determines the quality of excited state calculations, it is not always quite obvious. Therefore, another group of methods applied to real chemical objects and making use of the time-dependent density functional theory (TDDFT) formalism is presently actively developed [57–59].

Theoretically, these methods are based on the Runge–Gross theorem [58] which states that the exact time-dependent electron density of an interacting system determines the time-dependent external potential up to a certain constant. The search for solutions of the corresponding time-dependent Kohn–Sham equations is based on the variational principle according to which the variation of the action functional $A[\rho]$ for the exact electron density $\rho(r,t)$ should equal zero:

$$A[\rho] = \int_{t_0}^{t_1} dt \langle \Psi[\rho](r,\ t) i\hbar \frac{\partial}{\partial t} - H(t) \mid \Psi[\rho](T,\ t) \rangle,$$

$$\frac{\delta A[\rho]}{\delta \rho(r,\ t)} = 0. \tag{12}$$

where $\psi[\rho](r,\ t)$ and $\hat{H}(t)$ are the time-dependent wave function and full Hamiltonian of the system.

Thus, to calculate the electron density of an interacting system in the field of the external potential $\nu(r,\ t)_{\mathrm{ext}}$, to find the wave functions $\varphi_j(r,\ t)$ would suffice:

$$\rho(r,\ t) = \Sigma|\varphi_j(r,\ t)|^2. \tag{13}$$

In their turn, the $\varphi_j(r,t)$ functions are solutions of time-independent Kohn–Sham equations for a noninteracting system in the field of a certain effective potential $\nu_{\mathrm{eff}}[\rho](r,t)$:

$$i\hbar \frac{\partial}{\partial t} \varphi_j(r,\ t) = \left(-\frac{\hbar}{2m} \nabla^2 = v_{\mathrm{eff}}[\rho](r,\ t) \right) \varphi_j(r,\ t), \tag{14}$$

$$v_{\mathrm{eff}}[\rho](r,\ t) = v(r,\ t)_{\mathrm{ext}} + \int \frac{\rho(r',\ t)}{|r - r'|} d^3 r' + v_{xc}[\rho](r,\ t), \tag{15}$$

$$v_{xc}[\rho](r,\ t) = \frac{\delta A_{xc}[\rho]}{\delta \rho(r,\ t)}. \tag{16}$$

The $A_{xc}[\rho]$ and $\nu_{xc}[\rho](r,\ t)$ values represent the exchange-correlation part of the action functional and a potential whose exact expression is generally unknown. Within the adiabatic approximation, the exchange-correlation potential and its derivatives can be expressed through the time-independent exchange correlation energy $E_{xc}[\rho]$:

$$v_{xc}[\rho](r,\ t) \cong \frac{\delta E_{xc}[\rho]}{\delta \rho(r,\ t)},$$

$$\frac{v_{xc}[\rho](r,\ t)}{\delta \rho(r',\ t')} \cong \frac{\delta^2 E_{xc}[\rho]}{\delta \rho(r,\ t) \delta \rho(r',\ t')} \delta(t - t'). \tag{17}$$

Further on the $E_{xc}[\rho]$ energy is replaced by the exchange correlation energy of a static uniform electron gas (adiabatic local density approximation, ALDA)

$$E_{xc}^{\mathrm{LDA}}[\rho] = \int \varepsilon_{xc}[\rho(r)]\rho(r) d^3 r. \tag{18}$$

Here $\varepsilon_{xc}[\rho(r)]$ is the exchange-correlation energy per particle of a uniform electron gas.

Another widely used approximation partially includes the spatial nonuniformity of electron density (Generalized Gradient Approximation, GGA) [60–63]:

$$E_{xc}^{\mathrm{GGA}}[\rho] = \int f_{xc}[\rho(r),\ \nabla \rho(r)] d^3 r, \tag{19}$$

where $f[\rho(r^l,t),\nabla\rho(r^l,\ t)]$ is a certain semiempirical functional.

Since the exact exchange correlation potential is not known, various model functionals are used in practice, the most widespread of which include gradient-correlated BLYP [64, 65], BP86 [63, 66], PBE and its hybrid version PBE1PBE [66, 67], local functional SVWN [68], as well as three-parameter hybride functional B3LYP [69].

One the principal disadvantages of approximate exchange correlation functionals consists in their wrong asymptotic behavior. The case in point is that the Coulomb potential in Eq. (15) includes interaction of an electron with the full electron density, i.e. interaction of an electron not only with the rest electrons but also with itself. For an exact functional this effect should be completely compensated for by a contribution from exchange interactions responsible for its asymptotic behavior [70]. However, this is not the case with approximate functionals, which reveals itself in the above disadvantage.

If the time-dependent potential is sufficiently weak (the case of photoexcitation spectra), one can avoid complete numerical solution of the Kohn–Sham equation (14) and make use of the linear response theory

In terms of the TDDFT theory, the excitation energy is calculated considering the fact that the frequency-dependent linear response of a final system on perturbation produced by an external electromagnetic field has discrete poles in points corresponding to the excitation energies of the unperturbed system. Casida [71] showed that the task of searching for poles of the response function can be reduced to solution of eigenvalue equations written in matrix notation as

$$\begin{bmatrix} A & B \\ B^* & A^* \end{bmatrix}\begin{bmatrix} X \\ Y \end{bmatrix} = \omega\begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}\begin{bmatrix} X \\ Y \end{bmatrix}, \qquad (20)$$

$$A_{ia,jb} = \delta_{ij}\delta_{ab}(\varepsilon_i - \varepsilon_a) + (ia|jb) + (ia|f_{xc}|jb), \qquad (21)$$

$$B_{ia,jb} = (ia|bj) + (ia|f_{xc}|bj), \qquad (22)$$

A^* and B^* are the corresponding complex conjugate values.

In the adiabatic approximation, the $f_{xc}(r, r'; t - t') = \delta\nu_{xc}[\rho](r,t)/\delta\rho(r',t')$ functional called the exchange-correlation kernel is expressed through second derivatives of the exchange correlation energy (17). The eigenvalues and eigenvectors obtained from Eq. (20) correspond to the excitation energies and transition amplitudes.

For most valence states whose excitation energies lie well below the first ionization potential, TDDFT gives fairly accurate results (mean error ca. 0.2–0.3 eV). On the other hand, in cases where the approximate nature of the exchange-correlation functional takes significance, such deviations may prove much larger. This relates to states much contributed by double excitations, to charge transfer in spacially separated parts of large systems, to Rydberg states, and to systems with an extended π-electron system.

The accuracy of TDDFT methods for valence excited states are associated with the fact that the difference in the Kohn–Sham orbital energies which contribute most in the excitation energy is usually a very good approximation. This is because the virtual Kohn–Sham orbital energies are estimated for an *N*-electron system and, consequently, better correspond to the single-particle energy of an excited electron that the energy of an additional electron as in the HF theory, where the virtual orbital energies are estimated for an *N*+1-electron system.

The problem with Rydberg states can be associated with the wrong long-range asymptotic behavior of the approximate functional which decays exponentially at large distances. In this case, the results are much improved by the use of functionals with an asymptotically correct behavior [72–74].

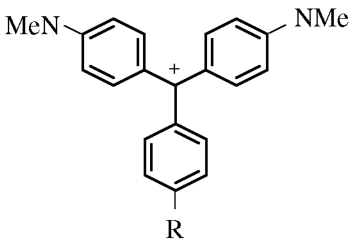
The errors in the description of quantum states contributed by double excitations are directly related to the fact that the linear response equations include exclusively singly excited states. A classical example of molecular systems with which wrong TDDFT results may occur is provided by polyynes whose low-lying singlet states are substantially contributed by double excitations. Evidence comes from the characteristics of two-photon absorption of these systems [75]. As shown by Mitra et al. [76], for adequate TDDFT description of double excitations of importance is to account for frequency dependence of the exchange-correlation kernel

Due to fairly low computing expenses combined with sufficient accuracy, TDDFT methods are used for calculating the spectra of a wide range of molecular systems.

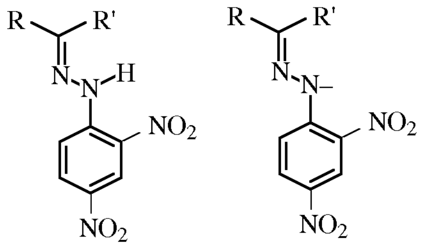
Guillaumont and Nakamura [77] studied the absorption spectra of industrial dyes: indigo, anthraquinone derivatives, naphthoquinone, azobenzene, cationic dyes, etc. The best fit to experiment was obtained by B3LYP hybrid functional calculations. The mean absolute deviation of the calculated from experimental values was 0.21 eV (6-31G basis); the maximum deviation was 0.56 eV for cationic dyes **II**.

With the basis set augmented by polarization and diffuse functions, markedly better results could only be obtained for hydrazones **III**. The worse reproduction of the transition energies of charged systems was explained by medium effects.

The mean absolute deviations of the B3LYP/6-31+G* energies of lower singlet transitions for a series of organic chromophores for experiment were 0.2–0.3 eV [78, 79]. An unexpectedly large deviation of



II



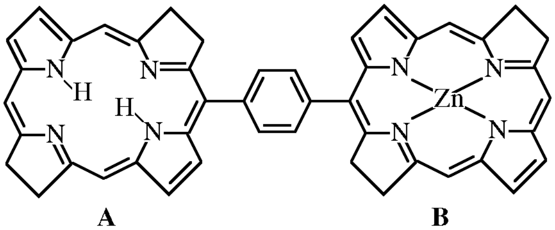
III

II, R = Cl, CN; **III**, R, R' = H, H; p-$NO_2C_2H_4$, CH_3; p-$NH_2C_2H_4$, CH_3.

0.7 eV for the $A'(\pi–\pi^*)$ transition energy was found for nitromethane.

The mean absolute deviations of the π□π* singlet transition (^1L_a and ^1L_b) energies in polycyclic aromatic hydrocarbons [80], calculated with the hybrid (B3LYP) and gradient-correlated (PB86) functionals with the cc-pVTZ basis set, were 0.23 и 0.13 eV for the first singlet transition (^1L_b) and 0.18 and 0.49 eV for the second transition (^1L_a), respectively. Such a large gap between the transition energies is associated with the fact that with the primarily ionic ^1L_a state one should account correctly for nonlocal effects which are better reproduced by the hybrid B3LYP functional that partially includes the HF exchange term. With triplet states, much smaller deviations were observed.

Underestimation of nonlocal properties of electron density is clearly illustrated by the results for states associated with charge transfer between spacially separated parts of a molecule [81–84]. A characteristic example is provided by the absorption spectra of zinc bacteriochlorin–bacteriochlorin com-plex **IV** [84]:



IV

According TD B3LYP/6-31G* calculations, the low-lying state with energies of 1.33, 1.46, 1.86, and 1.94 eV, arising in complex **IV,** are **B**→**A** charge-transfer in nature. The case in point is that the excitation energies of these states are mostly contributed by π–π* transitions, part of which relate to an electron delocalized in part **B** and the others, in part **A** of complex **IV**. The lowest excitation energy, qualitatively estimated from the calculated ionization potential of zinc bacteriochlorin (**B**), electron affinity of bacteriochlorin (**A**), and minimum distance between tetrapyrrole ring carbons, was 2.69 eV, which is double that calculated at the TDDFT level (1.3 eV). In such cases, the results can be improved by including the nonlocal HF exchange term in the unperturbed Hamiltonian [85, 86].

Along with the exchange correlation functional, TDDFT results are affected by structural characteristics of the ground electron state of a molecule [87]. Overestimation of π-electron delocalization (especially with “pure” DFT fucntionals), which affects bonds alternation in conjugated chains [88] and torsion angles in nonplanar systems, can introduce additional errors in excitation energies (of about several tenth of an eV) [89].

Completing consideration of methods for investigation of excited states of organic molecules, let us dwell shortly on a number of methods used in excited-state calculations: random phase approximation (RPA) [90, 91], second-order polarization propagator approximation (two-particle Green function) (SOPPA) [92–95], and algebraic diagrammatic construction (ADC) methods [96–101] in different approximations. These methods are all referred to as propagator methods which allow the energies and dipole moments of electron transitions to be obtained directly from ground-state dynamic polarizability expressions. The principal disadvantage of these methods is that it employs one-determinant approximation for calculation of multiconfiguration states.

The accuracy of the RPA method is fairly low. The absolute deviations of the calculated transition energies of the ${}^1B_{2u}$,${}^1B_{1u}$, and ${}^1E_{1u}$ states of benzene from experimental are 0.92, 0.32, and 0.56 eV, respectively. The SOPPA method that includes dynamic electron correlation effects in terms of the second-order perturbation theory provides much better results. The SOPPA energies of the same transitions are underestimated compared with experimental by 0.21, 0.19, and 0.19 eV, respectively [95].

The mean absolute error in the transition energies for the H_2O, HF, N_2, and Ne molecules, calculated by the ADC(2) method in which single excitations are described at the second-order and double excitations, at the zero-order perturbation theory level, is 0.64 eV at the maximum absolute error of 1.1 eV. With the ADC(3) scheme that includes single excitations at the third-order perturbation theory level, the mean absolute error is reduced to 0.17 eV and the maximum error, to 0.37 eV [99]. In terms of correctness and computing expences ($\sim N^6$, where N is the number of basis functions), ADC(3) compares with CCSD.

In conclusion we would like to give some general recommendations on excited-state calculations for molecular systems.

The choice of basis set depends on the concrete task. The minimal recommended basis can be a split valence basis including polarization functions for all atoms, except for hydrogen (6-31G* basis).For higher-order excitations and Rydberg states, additional diffuse functions should be included.

While not free from certain limitations, TDDFT methods can be considered optimal in terms of computing expenses ($\sim N^3$) and quality of results. Provided the functional and basis set for predominantly singly excited states are chosen properly, these methods compare in accuracy with theoretically more rigorous methods. Search for a universal exchange correlation functional that would allow excited states of different nature to be described with a high degree of accuracy is one of the most intriguing tasks in this field.

The CIS(D) method recommended by Grimme and Izgorodina [12] for excited-state calculations is, on the one hand, not free from drawbacks associated with the local nature and asymptotic behavior of the TDDFT functionals involves, one the other hand, problems concerning inclusion of dynamic correlation effects. Furthermore, the use of CIS(D) is also restricted by computing expenses that increase with system size as N^5.

Among methods based on the coupled-cluster formalism, the best results are provided by those including triple excitations, such as EOM-CCSD(T) or CC-3, whereas approximations including double excitations only (EOM-CCSD, CC2, or SAC-CI) can be considered as less effective. In view of huge computing expenses that tend to grow as N^6–N^7, these methods can be applied to molecular systems containing nearly 20 atoms. Moreover, the multiconfigurational nature of the ground electron state much reduces the accuracy of these methods. The same relates to the SOPPA and ACD(3) methods.

The optimal choice for systems with a multiconfigurational ground state is CASPT2 which is presently the most universal excited-state method. It is applicable for all molecular systems, whatever the nature of the ground and excited states.

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