Comparison of Multireference Møller−Plesset Theory and Time-Dependent Methods for the Calculation of Vertical Excitation Energies of Molecules[†]

Maja Parac and Stefan Grimme*

Organisch-Chemisches Institut der Universität Münster, Corrensstrasse 40, D-48149 Münster, Germany

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The vertical singlet−singlet excitation energies for a benchmark set of 14 medium and large molecules have been investigated with three quantum chemical methods. Calculations for electronic states with very different character in organic and inorganic systems are used to assess the accuracy and applicability of a simplified multireference Møller−Plesset (MR-MP2) approach, time-dependent density functional theory (TDDFT), and an approximate coupled cluster method with single and double excitations (CC2). In the pure ab initio approaches the resolution of the identity (RI) method for the calculation of the two-electron integrals is used to improve computational efficiency. It is shown that independently of the complexity of the electronic states involved, only the MR-MP2 method yields high accuracy (mean absolute deviation of 0.14 eV for 22 states). This finding is of particular importance because our scheme avoids computationally demanding orbital optimization steps and employs very compact reference wave functions. The TDDFT results are significantly poorer (mean absolute deviation of 0.26 eV), and systematic deviations for some $\pi \rightarrow \pi^*$ states, Rydberg states, and systems with unusual electronic structure are obtained. It is concluded that TDDFT has a potential for exploratory investigations or for very large molecules due to its computational efficiency. The CC2 method shows a tendency to overestimate excitation energies and is also limited to systems where the ground state is well described by a single determinant.

1. Introduction

The development of efficient algorithms and modern computer hardware within the past few decades has led to a dramatic progress in the scope and accuracy of quantum chemistry especially in the field of theoretical spectroscopy. However, the theoretical determination of electronic absorption spectra (e.g., UV−vis) for large molecules still remains a challenging goal for any quantum chemical method. The reason is that electronic structure methods which are able to provide high accuracy must include the nondynamical (near degeneracy) and dynamical electron correlation effects for states of often very different character in a balanced manner. One of the most popular approaches for that purpose is the CASPT2 method, where the nondynamical part of the correlation energy is recovered by the complete active space self-consistent field (CASSCF) method and the dynamic contribution is obtained by second-order perturbation theory.[1−5] A large body of successful CASPT2 applications to a variety of chemical problems has shown that low-order perturbation theory based on the Møller−Plesset[6] partitioning of the Hamiltonian yields very reliable results if the reference wave function provides a good zeroth-order description for the states of interest. However, one of the major limitations of the CASPT2 method is due to the CASSCF step, which requires the selection of a small number of active orbitals describing the nondynamical correlation. As for any full configuration interaction (CI) expansion, the CASSCF step becomes unmanageably large and impractical to handle when more than 12−14 electrons have to be included in the active space. This limitation is of crucial importance in the case of systems which necessarily require large active spaces, e.g., large unsaturated molecules, systems with low symmetry, or transition-metal compounds. Further problems arise when a larger number of states are desired because the (state-averaged) CASSCF procedure is then often difficult to converge.

To solve these problems and to push the limits of perturbation theory further, we have developed and implemented a general but simplified multireference second-order Møller−Plesset (MR-MP2) treatment based on restricted active space configuration interaction (RAS-CI) reference wave functions.[7] The method has been specially designed to perform parallel calculations on low-cost PC clusters for large molecules, and some successful applications have already been reported.[7−9] A similar but technically different approach has been proposed independently by Werner and Celani.[10]

In this paper we test the validity of our MR-MP2 method for the calculation of vertical singlet−singlet excitation energies (ΔE) for a benchmark set of molecules with very different types of electronic excitations. The systems considered have been carefully chosen such that (i) accurate experimental data are available and (ii) a very broad range of chemical structures with states of nontrivial electronic character is covered. In detail we present and discuss the data for the lowest-lying singlet excited states in the following molecules (see Chart 1): (i) $\pi \rightarrow \pi^*$ transitions in anthracene (**1**), indole (**2**), porphine (**3**), and indigo (**4**), (ii) $n \rightarrow \pi^*$ transitions in pyridazine (**5**), benzocyclobutenedione (**6**), benzaldehyde (**7**), and the cumulene C_5 (**8**), (iii) the low-lying valence states of main-group-element clusters P_4 (**9**) and Na_4 (**10**), (iv) excited states with d orbital participation in ferrocene ($Fe(C_5H_5)_2$, **11**) and chromium hexacarbonyl ($Cr(CO)_6$, **12**), and finally (v) Rydberg states in pyrrole (**13**) and hexamethyldisilane ($Si_2(CH_3)_6$, **14**).

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* To whom correspondence should be addressed. Fax: (+49) 251-83-33412. E-mail: grimmes@uni-muenster.de.

[†] Dedicated to Prof. S. D. Peyerimhoff on the occasion of her 65th birthday.

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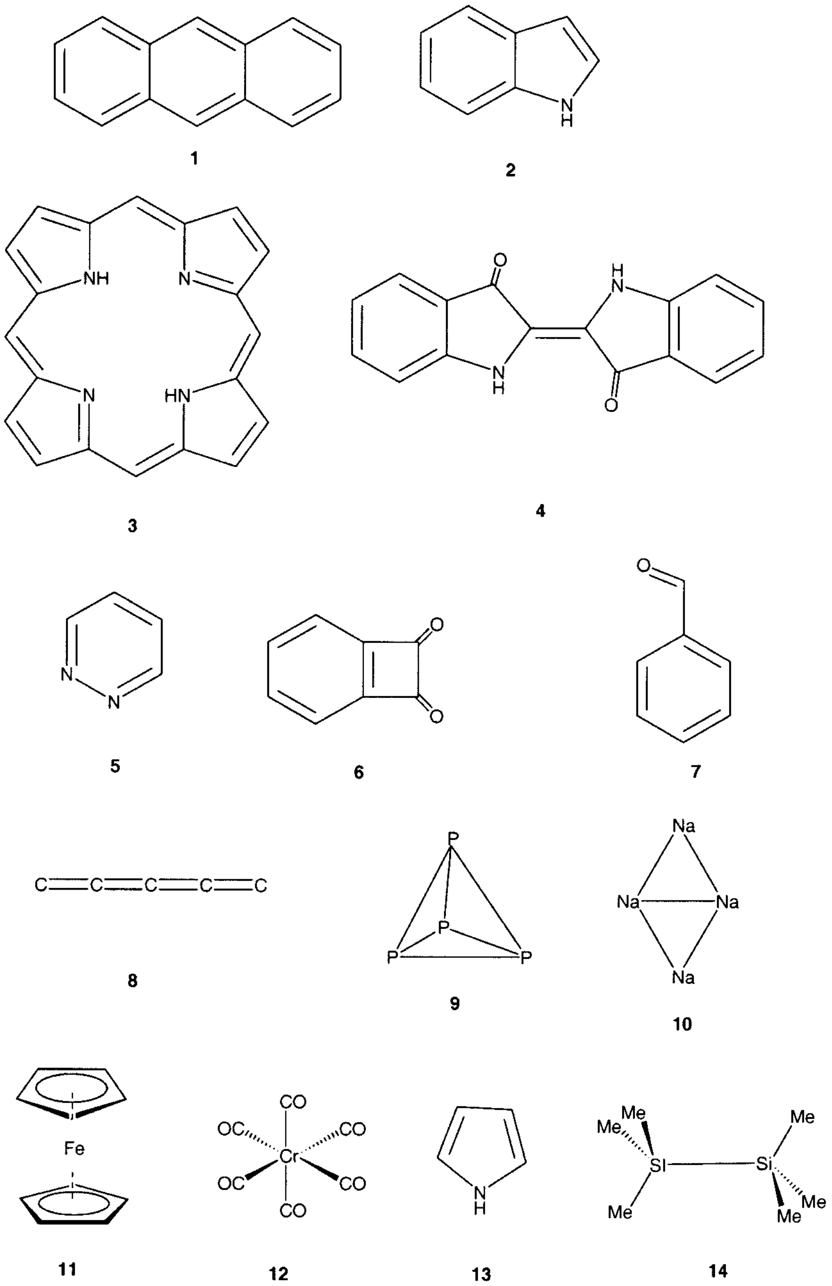
CHART 1: Structures of the Investigated Molecules



To learn more about the accuracy of other theoretical approaches which are applicable to large systems, we compare the MR-MP2 results to those from single-reference-based methods: the popular time-dependent density functional theory (TDDFT)[11] and a coupled cluster treatment with single and (approximate) double excitations (CC2).[12] Such comparisons are of particular importance if one should choose an accurate computational tool for an application on a large "real-life" problem. Although TDDFT requires less computational effort than the pure ab initio methods (formal scalings with system size are N_{el}^4 and N_{el}^5 for TDDFT and MR-MP2/CC2), our MR-MP2 and also the very efficient CC2 implementation of Hättig[13] are expected to be applicable to systems with several hundreds of electrons routinely. Thus, general considerations of accuracy and general applicability play an important role and will be discussed in detail in this paper.

In the next two sections we describe calculational details and discuss some important points which should be considered for an effective use of the MR-MP2 method for large systems. In section 4, results for the excitation energies are presented and discussed separately depending on the character of the particular excitation. In section 5, we summarize our conclusions concerning the applicability of the TDDFT, CC2, and MR-MP2 treatments to the problem of theoretical electronic spectroscopy.

2. Computational Details

All self-consistent field (SCF) and time-dependent calculations are performed with the TURBOMOLE package of programs.[14] The program modules escf[15] for TDDFT and cc2[13] for the coupled cluster treatment are used. The MR-MP2 calculations are performed in parallel with a code developed in our laboratory.[16,17] If not stated otherwise, Gaussian AO basis sets of valence triple-ζ quality augmented by polarization functions on all atoms (TZVP[18]) are used throughout our studies. Although larger AO basis sets could in principle be employed for almost all systems studied, we want to investigate the performance with basis sets which can be applied also for larger molecules. In the MR-MP2 and CC2 calculations the two-electron integrals are evaluated semidirectly with the resolution of the identity (RI) method.[7,13,19,20] In the RI method optimized auxiliary basis sets from the TURBOMOLE library are used.[21] For the calculations of Rydberg states, the TZVP basis sets are augmented with one set of sp(d) diffuse functions on each non-hydrogen atom ($\alpha_s = 0.03$ (C), 0.04 (N), 0.04 (P), 0.015 (Si); $\alpha_p = 0.03$ (C), 0.04 (N), 0.032 (P), 0.013 (Si); $\alpha_d = 0.01$ (Si)). In these cases the auxiliary basis sets are also augmented with an uncontracted function of the same angular momentum and a doubled exponent for each diffuse AO and one additional function with $l = l_{max} + 1$ ($\alpha_d = 0.06$ (C), 0.08 (N), 0.06 (P); $\alpha_f = 0.02$ (Si)). The errors for the excitation energies due to the RI approximation have been shown to be smaller than 0.02 eV.[7,13] The geometry optimizations for the ground states of the investigated molecules as well as the TDDFT computations are carried out with the B3-LYP hybrid functional,[22,23] which has been shown to outperform other functionals also for the prediction of excitation energies.[15] The ground-state geometries are employed throughout all excited-state calculations. Thus, the theoretical excitation energies correspond to vertical transitions which can be identified as band maxima in the experimental spectra. Although the uncertainties due to this approximation may reach 0.1−0.2 eV for the smaller compounds in our set, they are not expected to influence our general conclusions regarding the relative performance of the three theoretical models. In the CC2 and MR-MP2 correlation treatments core orbitals with orbital energies $< -2\ E_h$ and high-lying virtual MOs with orbital energies $> 5\ E_h$ are excluded while all single excitations are considered in TDDFT. In the CC2 and MR-MP2 calculations of the transition-metal compounds semicore 2s and 2p orbitals of Fe and Cr are treated as active orbitals. The truncation of the MR-MP2 first-order expansion space by configuration selection,[24] i.e., employing a diagonal approximation for the weakly interacting part, is performed using a selection threshold of $T_{sel} = 0.1\ \mu E_h$ as described in detail in ref 7.

3. Accuracy of Our Simplified MR-MP2 Method for Large Molecules

As mentioned in the Introduction, for an efficient treatment of large systems it is necessary to replace the computationally demanding orbital optimization (CASSCF) step by a simpler procedure. As one-particle basis in our MR-MP2 calculations we use Hartree−Fock self-consistent field (HF-SCF) orbitals optimized for the ground state of the system. Although in some cases other choices (e.g., open-shell SCF or improved virtual orbitals) give slightly better results, we want to show here that HF-SCF orbitals represent not only an economic but also a very accurate basis for MR-MP2 calculations. It should be emphasized here that our MR-MP2 method does not rely on a particular choice of the orbitals (opposed to CASPT2) and that CAS(RAS)SCF orbitals may be used in problematic cases.

Similar to the CASPT2 method, the accuracy of our MR-MP2 results critically depends on an appropriate choice of the zeroth-order wave function. We use excitation level restricted CI wave functions in a selected space of orbitals denoted as RAS(n, m, e_{max}), where n is the number of correlated electrons, m is the number of active orbitals, and e_{max} is the maximum allowed excitation level with respect to the closed-shell ground-state determinant. Regardless of the number of correlated electrons and active orbitals, the dimension of the reference wave function (and thus the computational effort) strongly depends on the chosen excitation level. Because this also affects the results, a compromise between accuracy and computational effort has to be found. Therefore, we first examine the influence of the reference space excitation level e_{max} on the calculated excitation energies for a selected subset of states. In Figure 1 we present calculated MR-MP2 excitation energies as a function of the chosen excitation level for the $2^1A'$ ($\pi \rightarrow \pi^*$, L_b), 1^1B_{2u} ($\pi \rightarrow \pi^*$), 1^1B_2 ($n \rightarrow \pi^*$), and 1^1B_{3u} excited states of indole, porphine, pyridazine, and Na_4, respectively.

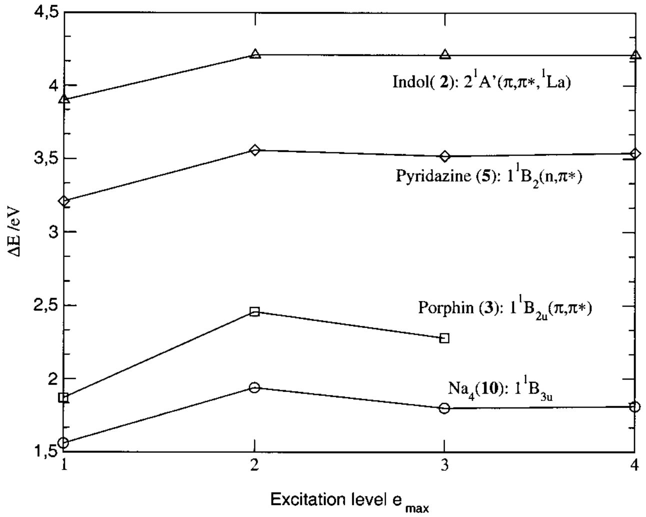


Figure 1. Dependence of the excitation energies for **2**, **5**, **3**, and **10** as a function of the chosen excitation level *l*.

In general, restriction to single excitations in the reference ($e_{max} = 1$) gives very poor results. The calculated values for the $2^1A'$ ($\pi \rightarrow \pi^*$, L_b) and 1^1B_{2u} states of indole and porphine are underestimated by almost 0.5 eV with respect to the experimental values of 4.4 eV[25−27] and 2.4 eV,[28] respectively. The ΔE values for the 1^1B_2 ($n \rightarrow \pi^*$) and 1^1B_{3u}(val) states of pyridazine and Na_4 are also underestimated by about 0.3 eV (experimental values are 3.4 eV[29] and 1.8 eV,[30] respectively). Increasing the excitation level to singles and doubles ($e_{max} = 2$) gives substantial improvement. All calculated excitation energies are now within 0.15 eV of the experimental values. Further enlarging the reference wave functions by including triple excitations ($e_{max} = 3$) yields a significant improvement only for two systems while additional quadruple excitations ($e_{max} = 4$) have almost no effect. On the basis of these results we adopt the following general procedure: the first MR-MP2 calculations, in which also the size of the necessary active space is determined, are performed with $e_{max} = 2$. If triple or higher excitations in the first-order-corrected wave functions show up with amplitudes above 0.04, the excitation level is increased only for the subset of the active orbitals connected with the corresponding excitations; i.e., we employ, e.g., RAS(n_1, m_1, 2) and RAS(n_2, m_2, 3) with $n_1 > n_2$ and $m_1 > m_2$.

As investigated previously,[10] a further reduction of the dimension of the reference wave function seems possible. The idea is based on the observation that even in an RAS reference wave function, most CI coefficients are very small. Thus, we include only those configurations in the reference for which their weight to any of the states of interest exceeds a certain threshold $T_{ref\ sel}$. In Figure 2 we demonstrate how this truncation influences the results. As examples, the 1^1B_u excited state of indigo and the 1^1B_2 and 1^1A_2 excited states of benzocyclobutenedione have been chosen.

Table 1 summarizes the results together with the number of reference configurations N_{ref} and the corresponding CPU time

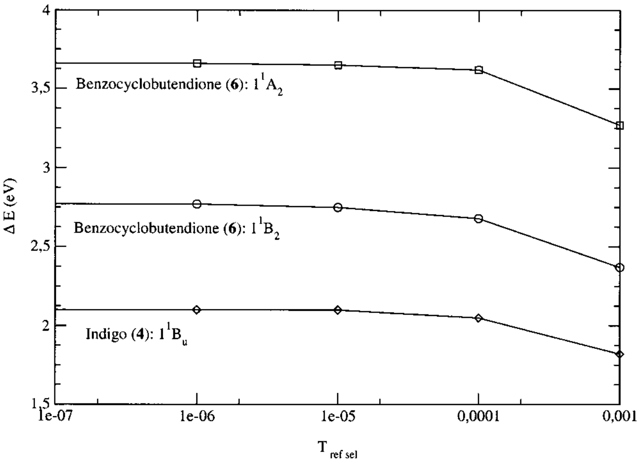


Figure 2. Dependence of the excitation energies for **6** and **4** as a function of the reference space selection threshold $T_{\text{ref sel}}$.

TABLE 1: Dependence of the Excitation Energies for the 1^1B_2 and 1^1A_2 States of Benzocyclobutenedione and the 1^1B_u State of Indole as a Function of $T_{\text{ref sel}}$

Benzocyclobutenedione

$T_{\text{ref sel}}$	N_{ref}[a]	Δ*E*, eV 1^1B_2	Δ*E*, eV 1^1A_2	CPU time, s
10^{-3}	94	2.37	3.27	252
10^{-4}	466	2.68	3.62	458
10^{-5}	1359	2.75	3.65	1312
10^{-6}	2468	2.77	3.66	2241
0	5287	2.77	3.66	8077
exptl[b]		2.8	3.5	

Indigo

$T_{\text{ref sel}}$	N_{ref}[a]	Δ*E*, eV 1^1B_u	CPU time, s
10^{-3}	64	1.82	2036
10^{-4}	319	2.05	3038
10^{-5}	670	2.10	4636
10^{-6}	909	2.10	5338
0	1049	2.10	7681
exptl[c]		2.0	

[a] N_{ref} is the number of reference configurations. [b] Experimental value taken from ref 39. [c] Experimental value taken from ref 36.

(time for a parallel job performed on eight PIII/800 processors). Calculations with nontruncated reference spaces ($T_{\text{ref sel}} = 0$) have been performed with 1049 (indigo) and 5287 (benzocyclobutenedione) configurations. It is seen that the use of $T_{\text{ref sel}} \leq 10^{-5}$ does not lead to any significant loss of accuracy. In the case of indigo use of this threshold reduces the dimension of the reference space and the CPU time required by a factor of about 1.7. For benzocyclobutenedione with the larger reference space the gain in efficiency is even more pronounced. N_{ref} is reduced by a factor of 4, and the CPU time decreases by a factor of 6. Although a further decrease of the threshold by one order of magnitude with minor loss in accuracy (<0.07 eV) seems possible, all other results have been obtained with $T_{\text{ref sel}} = 10^{-5}$. Test calculations on other systems (not shown) indicate that this choice ensures an overall accuracy of about 0.02−0.03 eV. It should be noted, however, that the errors introduced are quite systematic (underestimation of excitation energies) and that they are even smaller on a relative scale, i.e., when different excited states are compared. The systematic underestimation of the Δ*E* values when incomplete reference spaces are employed is a general feature of the MR-MP2 method. It can be traced back to its tendency to overestimate the correlation energies especially for the excited states which commonly have a more complicated structure than the ground state.

TABLE 2: Comparison of Calculated and Experimental Vertical Singlet−Singlet Excitation Energies

molecule	state	exptl energy,[a] eV	TDDFT error,[b] eV	CC2 error,[b] eV	MR-MP2 error,[b] eV
1	1^1B_{3u} ($\pi\pi^*$, L_a)	3.3	0.03	0.69	0.39
	1^1B_{2u} ($\pi\pi^*$, L_b)	3.5	0.42	0.43	−0.15
2	$2^1A'$ ($\pi\pi^*$, L_b)	4.4	0.52	0.53	−0.15
	$3^1A'$ ($\pi\pi^*$, L_a)	4.8	−0.02	0.47	0.15
3[c]	1^1B_{1u} ($\pi\pi^*$)	2.0	0.08	0.32	−0.33
	1^1B_{2u} ($\pi\pi^*$)	2.4	0.05	0.31	−0.07
	2^1B_{1u} ($\pi\pi^*$)	3.1	0.24	0.47	−0.03
	2^1B_{2u} ($\pi\pi^*$)	3.3	0.22	0.36	−0.02
4	1^1B_u ($\pi\pi^*$)	2.0	0.08	0.36	0.10
5	1^1B_2 (n → π^*)	3.4	0.14	0.47	0.22
6	1^1B_2 (n → π^*)	2.8	0.10	0.19	−0.12
	1^1A_2 (n → π^*)	3.5	0.05	0.33	0.12
7	$1^1A''$ (n → π^*)	3.8	−0.17	0.12	0.18
8	$^1\boldsymbol{\Pi}_u$ (n → π^*)	2.8	0.56	0.55	−0.19
9	1^1T_2	5.6	−0.27	**−0.08**	−0.22
10	1^1B_{3u}	1.8	0.06	0.03	0.05
11	1^1E_{1g} (d → d)	2.8	−0.79	−1.50[d]	0.05
12	1^1T_{1u} (d → π^*)	4.4	0.13	−0.44[d]	0.16
	2^1T_{1u} (d → π^*)	5.4	0.66	−0.74[d]	0.02
13	1^1A_2 (π → 3s)	5.2	−0.45	−0.06	0.06
	1^1B_2 (π → 3p)	5.8	−0.26	0.00	0.20
14	1^1E_u (σ → 4p)	6.4	−0.38	−0.68	0.12
mean dev			0.04	0.24	0.01
MAD			0.26	0.33	0.14

[a] Experimental data are taken from the compilations of references cited in the text and are rounded to one digit. [b] Error = Δ*E*(calcd) − Δ*E*(exptl). [c] SVP AO basis set[57] used in all porphine calculations. [d] These values are not included in the calculation of mean deviation and mean absolute deviation; see the text.

4. Results

In this section we discuss the results for the excitation energies (see Table 2) obtained with the MR-MP2, TDDFT, and CC2 methods for our benchmark set of molecules (for the structures see Chart 1). The molecules are grouped according to the nature of the particular excitation, which also guides our discussion of the data.

4.1. $\pi \rightarrow \pi^*$ States.

The first subset comprises organic molecules with extended π systems and $\pi \rightarrow \pi^*$ transitions. The optimized ground-state structures adopt planar geometries with D_{2h} (anthracene, **1**), C_s (indole, **2**), D_{2h} (porphine, **3**), and C_{2h} (indigo, **4**) symmetry. In the case of anthracene and indole we focus on two states labeled in the literature[31] as ^1L_a and ^1L_b, which are similar to those of, e.g., benzene and naphthalene. Depending on the relative energies of the corresponding orbitals and the molecular topology, the lowest excited singlet state either results from HOMO → LUMO (L_a) excitation or is due to the two nearly degenerate configurations: HOMO − 1 → LUMO and HOMO → LUMO + 1 (L_b). The ^1L_a and ^1L_b states have distinct properties: the L_a state has less multireference character (as indicated by a relatively large weight of double and higher excitations in the reference) but larger dynamical correlation contributions than the L_b state (vice versa). In the absorption spectrum of anthracene the more intense L_a (1^1B_{3u}) band is located at 3.31 eV.[32] The L_b (1^1B_{2u}) transition is hidden under the L_a band, and a considerable amount of effort has been undertaken to locate the L_b band experimentally.[33] The location of the L_a band of anthracene is predicted almost exactly with TDDFT, while CC2 and MR-MP2 overestimate the excitation energy by 0.69 and 0.39 eV, respectively. The L_b state is well described at the MR-MP2 level (3.35 eV), while CC2 and TDDFT overestimate ΔE by about 0.4 eV. This is in line with the larger multireference character of the L_b state, which cannot be described adequately by the single-reference methods which are expanded in a singles (TDDFT) or singles and doubles (CC2) basis. The ordering of the L_a and L_b states is correctly predicted by TDDFT, but CC2 and MR-MP2 predict the ^1L_a state to be above the ^1L_b state. A wrong ordering was also found in a MR-MP2 study with a CASSCF reference,[34] which indicates (together with results from an MR-MP4(SD) treatment[8]) that the restriction to second-order perturbation theory is responsible for this problem.

The gas-phase absorption spectrum of indole shows a low-intensity L_b band with a maximum at 4.37 eV and a more intense band identified as the L_a at 4.77 eV[25−27] (note the reverse state ordering compared to anthracene). The calculated errors for the two states are similar to those of anthracene. The CC2 method overestimates the transition energies, and the L_a band is calculated accurately with the TDDFT method. For indole, similarly to the CASPT2[35] study, our MR-MP2 method calculates the correct ordering for the L_b and L_a states and provides errors of less than 0.2 eV. This emphasizes our previous conclusion that the single-reference-based TDDFT and CC2 methods are not able to provide a good description for multiconfigurational L_b-type states.

As an example for a molecule with an extended π system we investigated free base porphine (FBP). The electronic spectrum of FBP is characterized by three regions:[28] a relatively weak Q band in the visible region split into two components, Q_x at 1.98−2.02 eV and Q_y at 2.33−2.42 eV; next follows the intense Soret or B region in the near-UV (3.13−3.33 eV) with two shoulders. We focus in our study on the position of the Q and B bands. The two lowest pairs of optically allowed states, $^1B_{1u}$–$^1B_{2u}$, could be assigned to each of the Q and B bands. The lowest excited singlet state is computed to be $1B_{1u}$. This state is well described by singly excited $\pi \rightarrow \pi^*$ configurations ($a_u \rightarrow b_{1g}$, $b_{3u} \rightarrow b_{2g}$). The second state of $1B_{2u}$ symmetry is dominated by singles arising from $a_u \rightarrow b_{2g}$ and $b_{3u} \rightarrow b_{1g}$ excitations. The third (fourth) valence excited state is $2B_{1u}$ ($2B_{2u}$), which is the plus (minus) combination of configurations corresponding to the minus (plus) $1B_{1u}$ ($1B_{2u}$) state. Except for the lowest lying state, which is computed to be too low by 0.33 eV, all states are described very well by the MR-MP2 method. A similar picture has been obtained in previous MR-MP2 and CASPT2 studies.[3,7,10] The TDDFT results for the two low-lying states are in excellent agreement with experimental data, while the two higher-lying states are overestimated by about 0.2 eV. As for the other $\pi \rightarrow \pi^*$ states, CC2 overestimates the excitation energies with slightly lower errors of about 0.3 eV for two low-lying states. The two high-lying states are overestimated by 0.4 eV.

As the last example in this section we discuss the excitation energy of the lowest-lying 1^1B_u ($\pi \rightarrow \pi^*$) state of the indigo dye, which is responsible for its blue color. This state mainly results from the HOMO → LUMO excitation. The MR-MP2 and TDDFT transition energies are in very good agreement (error of about 0.1 eV) with the experimental value[36] and previous CASPT2 results,[37] while it is again somewhat higher with CC2 (0.36 eV error).

4.2. n → π* States. In this section we expand our study to $n \rightarrow \pi^*$ excited states in pyridazine (**5**), benzocyclobutenedione (**6**), benzaldehyde (**7**), and C_5 (**8**). The ground-state geometries have been optimized within C_{2v} (**5** and **6**), C_s (**7**), and $D_{\infty h}$ (**8**) symmetry.

The lowest transition in pyridazine has been assigned as $n \rightarrow \pi^*$ with an absorption maximum at 3.4 eV.[29] Our MR-MP2 and TDDFT calculations confirm this assignment with errors for ΔE of 0.22 and 0.14 eV, respectively. Previous CASPT2 results[38] are also in good agreement with the experimental results. Although this state is dominated by single excitations, the CC2 value is found to be too high by 0.47 eV.

In the benzocyclobutenedione molecule with two carbonyl groups, two lowest-lying states of $n \rightarrow \pi^*$ type are considered. Because the transition to the 1^1A_2 state is symmetry forbidden and the transition to the 1^1B_2 state exhibits a low oscillator strength, they have not been observed in solid-state argon spectra.[39] However, both bands are clearly visible with vibrational structure at 2.79 eV (1^1B_2) and 3.49 eV (1^1A_2) in *n*-hexane solution. The agreement between calculated MR-MR2, TDDFT, and CC2 results and experiment is quite good with errors of −0.12, 0.19, and 0.10 eV, respectively, for the first state and 0.12, 0.33, and 0.05 eV for the second state.

The $1^1A''$ ($n \rightarrow \pi^*$) state of benzaldehyde represents a special case in our study because only the 0−0 transition located at 3.34 eV[40] has been established. The calculated vertical excitation energy can thus not directly be compared with the experimental number. In this case we correct the experimental adiabatic transition energy using the CASSCF difference between adiabatic and vertical excitation energies.[41] The MR-MP2, TDDFT, and CC2 results are then in good agreement (errors below 0.2 eV) with the estimated ΔE of 3.8 eV.

The highly unsaturated linear C_5 molecule represents one of the most unusual structures of the investigated systems. The low-lying Π_u state arises from excitations out of the two lone-pair orbitals located at the outer carbon atoms into antibonding π orbitals. Our MR-MP2 calculation confirms the assignment of this transition to a band observed experimentally around 2.8 eV, which is also in agreement with the result of MRCI calculations.[42] The TDDFT calculation employing the B3-LYP functional overestimates the excitation energy by 0.56 eV while results obtained with gradient-corrected nonhybrid functionals are much better (e.g., TDDFT/BP86[43,44] gives an error of only 0.09 eV). This is one of the frequently observed cases where the inclusion of "exact" Hartree−Fock exchange in the functional does not improve the results (e.g., the BH-LYP[45,46] functional with 50% HF exchange overestimates this excitation energy by more than 1 eV). The CC2 calculation for this state, like the TDDFT/B3-LYP case, overestimates the excitation energy by 0.55 eV.

4.3. Excited States Involving σ Orbitals. Main-group elements of the third or higher periods show a small tendency to form π bonds, and thus, three-dimensional σ-bonded structures are preferably built up. The excited states of such systems are often characterized by $n \rightarrow \sigma^*$ or $\sigma \rightarrow \sigma^*$ type excitations. It can be expected that in excited states of this type more electronic reorganization upon excitation occurs. We thus decided to include as examples one metallic (Na_4, **14**) and one covalently bound (P_4, **13**) cluster in our study. The geometry optimizations have been carried out within T_d (**13**) and D_{2h} (**14**) symmetry.

The first low-lying dipole-allowed transition in tetrahedral P_4 has been located at 5.6 eV.[46] This state results from HOMO → LUMO, LUMO + 1 excitations ($e \rightarrow t_1, t_2$). From previous studies on phosphorus clusters[47] it is known that this state has some Rydberg character and the calculations definitely require the inclusion of diffuse basis functions.

However, none of the three methods applied seems to have problems in the description of this state with some Rydberg/valence mixing: the errors are −0.27, −0.08, and −0.22 eV with TDFT, CC2, and MR-MP2 methods, respectively.

The excited states of sodium clusters of different size have been investigated in detail previously at the CI level.[48] As an example we have chosen the optically allowed $1B_{3u}$ state of the Na_4 cluster in its rhombus geometry. This state mainly consisits of a HOMO → LUMO + 1 ($b_{3u} \rightarrow a_g$) transition. The results obtained with all three methods are in excellent agreement (errors <0.1 eV) with the experimental value of 1.81 eV.[30]

4.4. Excited States Involving d Orbitals. Heretofore we have applied the different theoretical approaches to the calculation of electronic spectra of organic and main-group molecules. In this section we extend our study to low-lying excited states in transition-metal compounds, which remains a major challenge for computational chemistry. In general, near degeneracies within the d shells of transition metals cause a great importance of nondynamical correlation effects which are diffcult to describe with single-reference methods. In multireference-based methods one is faced with the problem of large active orbital spaces which often cannot be handeled by CASPT2. These systems furthermore represent a severe test for our MR-MP2 method because it is difficult to believe that the excited states can be described reasonably well using ground-state HF-SCF orbitals. As examples we consider here prototype systems with metals in low oxidation states: ferrocene ($Fe(C_5H_5)_2$, **11**) and octahedral chromium hexacarbonyl ($Cr(CO)_6$, **12**). The optimized structures have D_{5d} (**11**) and O_h (**12**) symmetry.

In ferrocene with D_{5d} symmetry, only transitions from the A_{1g} ground state to E_{1u} and A_{2u} states are dipole allowed. The lowest-lying transitions are dipole forbidden and acquire small transition probabilities through vibronic coupling as indicated by broad bands with small intensity. An excitation energy for the first $1E_{1g}$ state of 2.7 eV[49] has been reported. Meaningful results in this case could only be obtained with the MR-MP2 approach (error of −0.09 eV). The single-reference methods provide erroneous results: TDDFT underestimates this value by −0.79 eV and CC2 by −1.50 eV. CC2 results are very unstable and strongly dependent on the number of correlated core orbitals. In our calculations with active 2s and 2p shells, convergence problems for the second component of the E_{1g} state appeared.

As the second example we examined two dipole-allowed transitions in $Cr(CO)_6$. The electronic spectrum of $Cr(CO)_6$ is dominated by charge-transfer transitions from the metal 3d orbitals into the CO π^* orbitals, only $A_{1g} \rightarrow T_{1u}$ transitions of which are dipole allowed by symmetry. They appear in the spectra as two intense and broad bands with maxima at 4.43 and 5.41 eV.[50] Once more, reliable results are obtained only with the MR-MP2 method (errors of 0.16 and −0.12 eV for 1^1T_{1u} and 2^1T_1, respectively). The TDDFT method seems to be more robust and provides a reasonable description at least for the first state with an error of 0.13 eV, while the error for the 2^1T_{1u} state is as large as 0.6 eV. The CC2 results presented are again precarious due to the fact that the calculated ratio between the two oscillator strengths is in significant disagreement with the experimental finding.[50]

4.5. Rydberg States. So far we have considered valence excited states only. Excitations to orbitals with very large spatial extents are, however, ubiquitous and sometimes even lower-lying than valence states. To test the validity of the different theoretical approaches for electronic spectroscopy in general, we discuss in this section Rydberg-type excited states in pyrrole (**13**) and hexamethyldisilane ($Si_2(CH_3)_6$, **14**). The ground-state geometry optimizations have been carried out in C_{2v} (**13**) and D_{3d} (**14**) symmetry.

The spectrum of pyrrole is characterized by the appearance of a Rydberg series which overlaps bands arising from $\pi \rightarrow \pi^*$ valence states. Here we consider the first two low-lying Rydberg-type transitions observed at 5.22 and 5.82 eV.[51,52] According to the MR-MP2 and CC2 results, these transitions are assigned as $\pi \rightarrow 3s$ ($1A_2$) and $\pi \rightarrow 3p$ ($1B_2$) with errors in the calculated excitation energies of about 0.20 eV. Similar accuracy has been obtained also in previous coupled cluster[53] and CASPT2[54] studies. On the other hand, TDDFT underestimates both excitation energies by 0.45 and 0.26 eV. This can be attributed to the wrong asymptotic form of the density functional decaying too rapidly at large electron−nuclei distances.[55]

Although very different in structure, we obtain a similar picture for hexamethyldisilane. The first allowed Rydberg-type transition with $\sigma \rightarrow 4p$ character located experimentally at 6.35 eV[56] is considered. The MR-MP2 excitation energy agrees with experiment to within 0.12 eV, while TDDFT again underestimates this value by almost 0.4 eV. For unknown reasons, the CC2 method also provides very inaccurate results (error of −0.68 eV) in this case.

5. Conclusions

One multireference scheme (MR-MP2) and two single-reference methods (TDDFT and CC2) have been applied to the problem of the calculation of vertical excitation energies. The calculations have been performed for a set of diverse molecules with emphasis on the applicability and accuracy for the prediction of electronic spectra. It has been shown that the MR-MP2 method can be applied with good accuracy to almost any type of excited state. Opposed to the other two methods, the quality of the MR-MP2 results was found to be independent of the complexity of the electronic structure. The approximations introduced in our MR-MP2 approach (RI, truncation of reference wave functions, and use of HF-SCF orbitals) to perform efficient calculations for large sytems seem not to have any significant effect on the results. Although systems/states may exist where individual orbital optimizations are necessary, we have shown that a broad variety of problems in electronic spectroscopy can be solved efficiently using HF-SCF orbitals. If performed in parallel on a cheap Linux-PC cluster, MR-MP2 computations for systems with 100−200 electrons can be performed routinely within several hours of working time. The single-reference methods TDDFT and CC2 on the other hand have the advantage that they can be performed more or less in a “black-box” manner after an ordinary ground-state SCF calculation. The resulting disadvantage is, however, 2-fold. On the average, the accuracy for TDDFT and CC2 is lower (mean absolute deviation (MAD) of 0.26 and 0.33 eV vs 0.14 eV for MR-MP2), and a balanced description for all states cannot be achieved. The TDDFT method significantly over(under)estimates the excitation energies for L_b and Rydberg-type states. Larger errors are also found for transition-metal compounds and for the C_5 molecule. The CC2 method shows a tendency to overestimate $\pi \rightarrow \pi^*$ excitation energies (mean deviation of 0.24 eV compared to 0.04 and 0.01 eV for TDDFT and MR-MP2, respectively) and is not as robust as TDDFT to the degree of multireference character in the ground state. We thus finally conclude that MR-MP2 is still the method of choice for the calculation of electronic spectra, although TDDFT may also be useful after careful calibration for the systems under study or for exploratory investigations.

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