Treatment of electronic excitations within the adiabatic approximation of time dependent density functional theory

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Abstract

Time dependent density functional methods are applied in the adiabatic approximation to compute low-lying electronic excitations of N_2, ethylene, formaldehyde, pyridine and porphin. Out of various local, gradient-corrected and hybrid (including exact exchange) functionals, the best results are obtained for the three-parameter Lee–Yang–Parr (B3LYP) functional proposed by Becke. B3LYP yields excitation energies about 0.4 eV too low but typically gives the correct ordering of states and constitutes a considerable improvement over HF-based approaches requiring comparable numerical work.

1. Introduction

A reliable quantum mechanical treatment of electronic excitation in atoms and molecules requires in general a proper inclusion of static and dynamic effects of electron correlation. This makes it necessary to carry out extended multiple reference (MR) configuration interaction (CI) type calculations – such as MR-CI [1] itself or CAS-PT2 [2], complete active space plus perturbation theory in second order – to reach an accuracy of about 0.1 eV in excitation energies. The same accuracy is achieved by EOM-CC (equation of motion coupled cluster) [3] treatments provided the ground state is of single reference type and the excited state is dominated by a single excitation from the ground state. In this case one could also hope that much less expensive SCF-type (SCF: self-consistent field) approximations, e.g. singles CI (SCI) [4] or RPA (random phase approximation) [5] would suffice but these methods appear to work satisfactorily only in special cases (see e.g. Ref. [6]).

Since DFT (density functional theory) methods rectify many problems of the SCF approximation at comparable or even lower computational cost, there is currently great interest in extending DFT to the treatment of excitations. The foundation of DFT is tightly coupled to the consideration of ground states and static external potentials. For an extension of the theory to the treatment of time dependent scalar and/or vector potentials the reader is referred to the review by Gross and Kohn [7]. A time dependent formalism opens the way to the computation of frequency dependent response functions, such as the dynamic polarizability $\alpha(\omega)$, and excitation energies which are characterized as the poles of the response quantities.

Applications of the time dependent density functional theory (TDDFT) in the field of quantum chemistry have recently been reported by van Gisbergen et al. [8] and Jamorski et al. [9] who implemented a time dependent Kohn–Sham (TDKS) scheme for the calculation of dynamic polarizabilities and by Petersilka et al. [10] who presented a method for the calculation of excitation energies by systematic improvement upon the poles of the Kohn–Sham response function. Jamorski et al. also calculated the poles of the response function and implemented a scheme for the calculation of excitation energies. For a largely self-contained review of TDDFT from the point of view of quantum chemistry the reader is referred to an article by Casida [11].

It is a discomforting feature of DFT that the exact form of the exchange–correlation functional $E_{xc}[\rho]$ is not known. Nevertheless a great variety of applications has shown that the method is robust in the sense that a number of approximate forms for E_{xc} lead to useful results. In TDDFT the situation is aggravated by the fact that $A_{xc}[\rho]$, the time dependent analogue of E_{xc}, is a functional of the time dependent electron density $\rho(r, t)$ whereas E_{xc} depends only on the stationary $\rho(r)$. The conceptually most simple ansatz, the so-called adiabatic approximation, is used in the applications cited above as well as in the present work. This approximation amounts to using the zero-frequency limit of A_{xc} for treatments of finite frequency perturbations which is certainly justified in the low-frequency domain. It is however not clear to what extent it is valid for the calculation of excitation energies. In this context we present an extended test of the adiabatic approximation in the calculation of DFT excitation energies. We go beyond the local density approximation (LDA) and include the commonly used gradient corrections which yield markedly more accurate results for ground state properties. As the time dependent Hartree–Fock (TDHF) scheme can be derived along the same lines as TDDFT [11] we do not hesitate also to include one of the hybrid functionals proposed by Becke [12] in our study. The latter seems especially promising because of the good performance of these functionals in static polarizability calculations [1].

2. Theory

In this section we essentially rederive the expressions already presented in Refs. [7] and [11] in order to document the working equations for our computational approach.

The time dependent extensions of the Hohenberg–Kohn theorems due to Gross and Runge can be used to construct a TDKS scheme [14,7]. In this scheme the interacting system subject to a time dependent external potential

$$v_e(r, t) = v_{stat}(r) + v_t(r)f(t) \tag{1}$$

is mapped onto a noninteracting model system. For the latter, a time dependent potential $v_{KS}(r, t)$ is derived such that its density $\rho(r, t)$ becomes identical to the density of the interacting system.

The noninteracting system is described by the Schrödinger equation

$$i\frac{\partial}{\partial t}\varphi_i(r, t) = \left(-\frac{\nabla^2}{2} + v_{KS}(r, t)\right)\varphi_i(r, t), \tag{2}$$

where $v_{KS}(r, t)$ is given by

$$v_{KS}(r, t) = v_e(r, t) + \int d^3r' \frac{\rho(r', t)}{|r - r'|} + \frac{\delta A_{xc}[\rho]}{\delta\rho(r, t)}. \tag{3}$$

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[1] This has been pointed out in Ref. [13] and verified in own calculations.

The time dependent exchange–correlation functional $A_{xc}[\rho]$ is the analogue of $E_{xc}[\rho]$ in the static case; it is a functional of the density as a function of space and time. In the adiabatic (low frequency) limit the approximation

$$A_{xc}[\rho] = \int dt\, E_{xc}[\rho]\big|_{\rho=\rho(r,\,t)} \tag{4}$$

is reasonable and will be used throughout this paper to establish its validity. For a more general treatment concerning $A_{xc}[\rho]$ the reader is referred to Refs. [11] and [7]. The adiabatic approximation for $A_{xc}[\rho]$ is local in time – it leads to a contribution to $v_{KS}(r, t)$ which depends only on ρ at time t.

To treat the time dependent response of the interacting system we consider a situation in which the system was initially in its ground state and the time dependent part of v_e has been switched on adiabatically. In this case the first order density response $\rho^{(1)}$ is described by the linear response kernel $\chi(t, t', r, r')$ of the interacting system. Alternatively the density response can be described by $\chi_{KS}(t, t', r, r')$, the linear response kernel of the noninteracting (Kohn–Sham) system. In this case, however, it has to be noted that the response is not to v_t but to $v_{KS}^{(1)}$, the Kohn–Sham potential up to the first order in v_t. The latter depends on v_t as well as on the density response $\rho^{(1)}$ itself which leads to a self-consistent scheme for the calculation of $\rho^{(1)}$. The great advantage of this procedure is that $\chi_{KS}(t, t', r, r')$ as a noninteracting response function is easy to calculate.

We thus find the following equation for $\rho^{(1)}$ [7],

$$\rho^{(1)}(r, t) = \int d^3r'\, dt'\, \chi_{KS}(t, t', r, r')\left[v_t(r')f(t') + \int d^3r'' \frac{\rho^{(1)}(r'', t')}{|r' - r''|} \right.$$

$$\left. + \int d^3r'' \frac{\delta^2 E_{xc}}{\delta\rho(r')\delta\rho(r'')}\rho^{(1)}(r'', t') \right]. \tag{5}$$

By use of the Fourier transform, $f(\omega) = \int e^{i\omega t}f(t)\, dt$, Eq. (5) becomes

$$\rho^{(1)}(r, \omega) = \int d^3r'\, \chi_{KS}(\omega, r, r')\left[v_t(r')f(\omega) + \int d^3r'' \frac{\rho^{(1)}(r'', \omega)}{|r' - r''|} \right.$$

$$\left. + \int d^3r'' \frac{\delta^2 E_{xc}}{\delta\rho(r')\delta\rho(r'')}\rho^{(1)}(r'', \omega) \right]. \tag{6}$$

To find a self-consistent solution for $\rho^{(1)}(r, \omega)$ we use the parametrization

$$\rho_\sigma^{(1)}(r, \omega) = \sum_{i,a,\sigma} \left[P_{ia\sigma}(\omega)\phi_{a\sigma}^*(r)\phi_{i\sigma}(r) + P_{ai\sigma}(\omega)\phi_{a\sigma}(r)\phi_{i\sigma}^*(r) \right], \tag{7}$$

with the ground state Kohn–Sham orbitals $\phi_{k\sigma}(r)$. In our notation the indices i, j and a, b stand for occupied and virtual orbitals respectively, the indices k, l, m, n denote general orbitals. We have introduced the spin variable $\sigma(\sigma = \alpha, \beta)$ to account for spin dependent external potentials as well as for the fact that the approximations available for $E_{xc}[\rho]$ depend on the spin densities ρ_α and ρ_β. With the expression for $\chi_{KS,\sigma\sigma'}(\omega, r, r')$,

$$\chi_{KS,\sigma\sigma'}(\omega, r, r') = \delta_{\sigma\sigma'}\sum_{i,a}\left(\frac{\phi_{i\sigma}^*(r)\phi_{a\sigma}(r)\phi_{i\sigma}(r')\phi_{a\sigma}^*(r')}{\omega - (\epsilon_{a\sigma} - \epsilon_{i\sigma})} \right.$$

$$\left. - \frac{\phi_{i\sigma}(r)\phi_{a\sigma}^*(r)\phi_{i\sigma}^*(r')\phi_{a\sigma}(r')}{\omega + (\epsilon_{a\sigma} - \epsilon_{i\sigma})} \right), \tag{8}$$

(for a derivation see e.g. Ref. [11]) and

$$(v_t)_{ia\sigma} = \int d^3 r \; \phi^*_{i\sigma}(r) v_t(r) \phi_{a\sigma}(r) \tag{9}$$

one obtains two coupled matrix equations for $P_{ia\sigma}(\omega)$ and $P_{ai\sigma}(\omega)$,

$$\left[\delta_{\sigma\tau} \delta_{ij} \delta_{ab} (\epsilon_{a\sigma} - \epsilon_{i\sigma} + \omega) + K_{ia\sigma,jb\tau} \right] P_{jb\tau} + K_{ia\sigma,bj\tau} P_{bj\tau} = -(v_t)_{ia\sigma}, \tag{10}$$

$$\left[\delta_{\sigma\tau} \delta_{ij} \delta_{ab} (\epsilon_{a\sigma} - \epsilon_{i\sigma} - \omega) + K_{ai\sigma,bj\tau} \right] P_{bj\tau} + K_{ai\sigma,jb\tau} P_{jb\tau} = -(v_t)_{ai\sigma}, \tag{11}$$

where the matrix **K** is given by

$$K_{kl\sigma,mn\tau} = \int d^3 r \; d^3 r' \; \phi^*_{k\sigma}(r) \phi_{l\sigma}(r) \left(\frac{1}{|r - r'|} + \frac{\delta^2 E_{xc}}{\delta \rho_\sigma(r) \delta \rho_\tau(r')} \right) \phi^*_{n\tau}(r') \phi_{m\tau}(r'). \tag{12}$$

Adopting the commonly used notation $X_{ia\sigma} = P_{ia\sigma}(\omega)$, $Y_{ia\sigma} = P_{ai\sigma}(\omega)$ and $V_{ia\sigma} = (v_t)_{ia\sigma}$, the coupled matrix equations can be written in the condensed form

$$\left[\begin{pmatrix} \mathbf{L} & \mathbf{M} \\ \mathbf{M}^* & \mathbf{L}^* \end{pmatrix} - \omega \begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix} \right] \begin{pmatrix} \mathbf{X} \\ \mathbf{Y} \end{pmatrix} = -f(\omega) \begin{pmatrix} \mathbf{V} \\ \mathbf{V}^* \end{pmatrix}, \tag{13}$$

with

$$L_{ia\sigma,jb\tau} = \delta_{\sigma\tau} \delta_{ij} \delta_{ab} (\epsilon_{a\sigma} - \epsilon_{i,\sigma}) + K_{ia\sigma,jb\tau}, \tag{14}$$

$$M_{ia\sigma,jb\tau} = K_{ia\sigma,bj\tau}. \tag{15}$$

Excitation energies, which in response theory are characterized as the poles of the response functions, lead to zero eigenvalues of the matrix on the left hand side of Eq. (13). They can thus be determined as solutions of the non-Hermitian eigenvalue problem

$$\begin{pmatrix} \mathbf{L} & \mathbf{M} \\ \mathbf{M}^* & \mathbf{L}^* \end{pmatrix} \begin{pmatrix} \mathbf{X} \\ \mathbf{Y} \end{pmatrix} = \omega \begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix} \begin{pmatrix} \mathbf{X} \\ \mathbf{Y} \end{pmatrix}, \tag{16}$$

which has the same structure as the eigenvalue problem resulting from the RPA within HF theory. Properties of the solutions of Eq. (16) are extensively discussed in the literature (see e.g. Ref. [15] or Ref. [16]).

If we start from a restricted KS calculation which implies $\phi_{m\alpha} = \phi_{m\beta}$ (and hence $\rho_\alpha = \rho_\beta$) we can use the unitary transformation

$$u_{ia} = \frac{1}{\sqrt{2}} (P_{ia\alpha} + P_{ia\beta}), \tag{17}$$

$$v_{ia} = \frac{1}{\sqrt{2}} (P_{ia\alpha} - P_{ia\beta}), \tag{18}$$

to discriminate between excitations which keep the constraint $\rho_\alpha = \rho_\beta$ (singlet excitations) or break it (triplet excitations). As in the HF case [17] the resulting matrices $\mathbf{L}^p$, $\mathbf{M}^p$ ($p = s, t$; singlet or triplet) are closely related to the triplet and singlet instability matrices which we derived in a previous paper [18]. Explicit expressions for $\mathbf{L}^p$ and $\mathbf{M}^p$ are given in the Appendix.

In quantum chemistry the orbitals $\phi_{k\sigma}$ can usually be chosen real. This leads in the adiabatic approximation to real expressions for the matrices $\mathbf{L}^p$ and $\mathbf{M}^p$. The eigenvalue problem Eq. (16) can then be transformed to (see e.g. Ref. [16])

$$(\mathbf{M}^p - \mathbf{L}^p)(\mathbf{M}^p + \mathbf{L}^p)(\mathbf{X} + \mathbf{Y}) = \omega^2 (\mathbf{X} + \mathbf{Y}) \tag{19}$$

which reduces its dimension by a factor of two. Nevertheless the matrix product on the left hand side of Eq. (19) remains non-Hermitian. If $\mathbf{M}^P - \mathbf{L}^P$ is positive definite, Eq. (19) can be further transformed into the Hermitian eigenvalue equation

$$(\mathbf{M}^P - \mathbf{L}^P)^{1/2}(\mathbf{M}^P + \mathbf{L}^P)(\mathbf{M}^P - \mathbf{L}^P)^{1/2}(\mathbf{X} + \mathbf{Y})' = \omega^2(\mathbf{X} + \mathbf{Y})', \tag{20}$$

with

$$(\mathbf{X} + \mathbf{Y})' = (\mathbf{M}^P - \mathbf{L}^P)^{-1/2}(\mathbf{X} + \mathbf{Y}). \tag{21}$$

Since in TDDFT the matrix $(\mathbf{M}^P - \mathbf{L}^P)$ is purely diagonal with diagonal elements $\epsilon_a - \epsilon_i$, Eq. (20) becomes particularly simple in this case. For the calculation of excitations from the ground state, the positive definiteness of $(\mathbf{M}^P - \mathbf{L}^P)$ is guaranteed as long as the aufbau principle is not violated [18]. Note that this is not generally true in TDHF, where $(\mathbf{M}^P - \mathbf{L}^P)$ has a more complicated structure.

For the solution of the eigenvalue problem Eq. (20) we used the iterative subspace method as implemented in the escf program of the TURBOMOLE package [19]. Alternatively we used a modified Davidson algorithm [20] especially designed for the direct solution of Eq. (16). For the calculations using the hybrid functional only the latter approach was taken since the matrix $(\mathbf{M}^P - \mathbf{L}^P)$ is not purely diagonal in this case.

The computationally most demanding step in these algorithms is the calculation of matrix-(test)-vector products. To avoid explicit calculation and storage of the generally very large matrices as well as to avoid four index transformations from the basis function to the molecular orbital (MO) representation, the matrix vector multiplication is directly done in the basis function representation [19]. Further technical details are as described in Ref. [18].

3. Applications

As a test of the approach described above, we calculated the lowest excitation energies of N_2, formaldehyde, ethylene, pyridine and porphin. Comparisons between the following approximations of the exchange correlation functional were carried out: the local functional S-VWN [21,22], the gradient corrected functionals B-LYP [23,24] and B-P [23,25] and the hybrid functional B3LYP (see e.g. Ref. [26] for a description of B3LYP). Additionally the HF based SCI and RPA methods were used to allow a comparison with traditional methods of comparable computational cost.

We chose the Sadlej basis set [27] for all calculations except those on porphin where we used a smaller SVP (split valence plus polarization [28]) basis. Sadlej has designed the basis set for an accurate description of static polarizabilities (which requires rather diffuse functions), and this should also be appropriate in the low-frequency regime. To get an estimate of the quality of our basis set, we compared our results to the ones obtained by Pople et al. [4] for SCI calculations on ethylene and formaldehyde. Except for the relatively high lying triplet and singlet A_g states of ethylene, where we found a deviation of about 0.5 eV, all other results agreed within 0.1 eV. Pople et al. used a 6-31 + G* basis set, especially designed for the calculation of anions, which they augmented by an additional diffuse sp-shell to account for Rydberg states.

For structures, orientations and references to experimental data of formaldehyde, ethylene and pyridine the reader is, unless otherwise noted, referred to Ref. [4] where these molecules were taken as benchmarks for the SCI method. In the calculations on porphin we used the MP2 (DZP) optimized D_{2h} structure published in Ref. [29] with the molecule in the yz-plane and the z-axis going through two H and two N atoms; this fixes the assignment of irreducible representations. The calculations on N_2 were done at the internuclear equilibrium distance of 109.77 pm [30].

The results of our calculations for the S-VWN, B-P and B3LYP functionals as well as the results obtained from SCI and RPA are presented in Tables 1–5. For the smaller molecules we calculated the mean, mean absolute, root mean square (rms) and maximum deviation of calculated excitation energies from the experimen-

Table 1
Computed vertical excitation energies for N_2 in comparison to experiment

Transition		Excitation energy (eV)					
		S-VWN	B-P	B3LYP	SCI	RPA	exp. [a]
$^1\Delta_u$	$\pi_u \rightarrow \pi_g$	10.22	10.04	9.73	9.06	8.78	10.27
$^1\Sigma_u^-$	$\pi_u \rightarrow \pi_g$	9.65	9.66	9.32	8.50	7.94	9.97
$^1\Pi_g$	$\sigma_g \rightarrow \pi_g$	9.05	9.11	9.25	10.02	9.77	9.31
$^3\Pi_u$	$\sigma_u \rightarrow \pi_g$	10.36	10.38	10.62	11.74	11.28	11.19
$^3\Sigma_u^-$	$\pi_u \rightarrow \pi_g$	9.65	9.66	9.32	8.50	7.94	9.67
$^3\Delta_u$	$\pi_u \rightarrow \pi_g$	8.82	8.24	7.97	7.33	5.86	8.88
$^3\Pi_g$	$\sigma_g \rightarrow \pi_g$	7.54	7.37	7.55	7.99	7.62	8.04
$^3\Sigma_u^+$	$\pi_u \rightarrow \pi_g$	7.86	7.40	7.04	6.23	3.46	7.75
Statistics							
mean dev.		− 0.24	− 0.40	− 0.54	− 0.71	− 1.55	
mean abs. dev.		0.27	0.40	0.54	1.03	1.69	
rms dev.		0.38	0.48	0.59	1.15	2.16	
max. dev.		0.83	0.81	0.91	1.55	4.29	

[a] Taken from Ref. [31].

tal values. Results obtained from the functional B-LYP will not be documented since they are roughly comparable to B-P. In Table 6 we present a statistical analysis of the collected data for N_2, formaldehyde, ethylene and pyridine.

One reason for our calculations on the N_2 molecule was to check the validity of our implementation. Since we used the same basis set and geometry as Jamorski et al. [9] our results for the S-VWN functional can be directly compared to their work. Both results are found to agree within 0.02 eV. This insignificant deviation could for example be caused by the use of an auxiliary basis in [9] whereas we treated Coulomb terms without approximations.

Comparing the results obtained with the gradient corrected B-P functional to those obtained with the local S-VWN approximation shows that the gradient correction does not give a marked improvement. On the contrary, the rms deviation of the B-P results is slightly poorer than for S-VWN. The results obtained with the B3LYP functional suffer from the relatively poor description of the $^3\Sigma_u^+$ state which is related to the near

Table 2
Computed vertical excitation energies for formaldehyde in comparison to experiment

Transition		Excitation energy (eV)					
		S-VWN	B-P	B3LYP	SCI	RPA	exp.
$^1B_1$	$\sigma \rightarrow \pi^*$	8.70	8.79	8.93	9.83	9.59	9.0
$^1A_1$	$n \rightarrow 3p$	6.79	6.76	7.30	9.53	9.19	8.14
$^1B_2$	$n \rightarrow 3s$	5.93	5.97	6.45	8.60	8.60	7.13
$^1A_2$	$n \rightarrow \pi^*$	3.64	3.80	3.88	4.55	4.37	4.1
$^3B_2$	$n \rightarrow 3s$	5.86	5.85	6.32	8.24	8.16	7.09
$^3A_1$	$\pi \rightarrow \pi^*$	6.11	5.60	5.32	4.85	1.87	6.0
$^3A_2$	$n \rightarrow \pi^*$	3.02	3.05	3.14	3.72	3.40	3.5
Statistics							
mean dev.		− 0.70	− 0.73	− 0.52	0.62	0.03	
mean abs. dev.		0.74	0.73	0.52	0.95	1.24	
rms dev.		0.87	0.87	0.59	1.05	1.77	
max. dev.		1.36	1.38	0.84	1.47	4.13	

Table 3

Computed vertical excitation energies for ethylene in comparison to experiment

Transition		Excitation energy (eV)					
		S-VWN	B-P	B3LYP	SCI	RPA	exp.
^1A_g	$\pi \to 3p\pi$	8.24	8.17	8.19	8.62	8.57	8.29
$^1B_{2g}$	$\pi \to 3p\sigma$	7.21	7.11	7.17	7.92	7.92	8.0
$^1B_{1u}$	$\pi \to \pi^*$	7.45	7.40	7.36	7.71	7.35	≈ 8.00 [a]
$^1B_{1g}$	$\pi \to 3p\sigma$	7.22	7.17	7.19	7.76	7.75	7.83
$^1B_{3u}$	$\pi \to 3s$	6.66	6.62	6.61	7.15	7.14	7.15
^3A_g	$\pi \to 3p\pi$	8.00	7.91	7.90	8.02	7.97	8.15
$^3B_{1g}$	$\pi \to 3p\sigma$	6.96	7.06	7.13	7.66	7.63	7.79
$^3B_{2g}$	$\pi \to 3p\sigma$	7.15	7.05	7.10	7.80	7.76	7.79
$^3B_{3u}$	$\pi \to 3s$	6.59	6.53	6.52	6.92	6.88	6.98
$^3B_{1u}$	$\pi \to \pi^*$	4.62	4.11	3.99	3.55	0.26	4.36
Statistics							
mean dev.		−0.42	−0.52	−0.52	−0.12	−0.51	
mean abs. dev.		0.48	0.52	0.52	0.19	0.57	
rms dev.		0.54	0.58	0.56	0.30	1.32	
max. dev.		0.83	0.89	0.83	0.81	4.10	

[a] Estimated from theoretical work [2].

Table 4

Computed vertical excitation energies for pyridine in comparison to experiment

Transition		Excitation energy (eV)					
		S-VWN	B-P	B3LYP	SCI	RPA	exp.
$^1A_1$	$\pi \to \pi^*$	6.16	6.15	6.19	6.45	6.12	6.38
$^1A_2$	$n \to \pi^*$	4.29	4.45	5.07	6.79	6.79	5.43
$^1B_2$	$\pi \to \pi^*$	5.35	5.34	5.47	6.10	5.85	4.99
$^1B_1$	$n \to \pi^*$	4.20	4.34	4.76	6.16	5.99	4.59
$^3A_2$	$n \to \pi^*$	4.18	4.31	4.93	6.66	6.64	5.40
$^3B_2$	$\pi \to \pi^*$	4.52	4.39	4.47	4.63	4.30	4.84
$^3A_1$	$\pi \to \pi^*$	4.48	4.06	3.91	3.53	4.79	4.1
$^3B_1$	$n \to \pi^*$	3.67	3.70	4.05	5.12	4.82	4.1
Statistics							
mean dev.		−0.37	−0.38	−0.12	0.70	0.68	
mean abs. dev.		0.56	0.47	0.29	0.90	0.88	
rms dev.		0.67	0.59	0.32	1.04	0.96	
max. dev.		1.22	1.09	0.48	1.57	1.40	

Table 5

Computed vertical excitation energies for porphin in comparison to experiment

State	Excitation energy/eV						
	S-VWN	B-P	B3LYP	SCI	RPA	CAS-PT2 [a]	exp. [b]
$^1B_{1u}$	2.18	2.17	2.27	2.41	1.72	1.70	2.01
$^1B_{2u}$	2.32	2.30	2.43	2.53	1.89	2.26	2.38
$^1B_{1u}$	2.99	2.98	3.32	4.48	3.95	2.91	3.1
$^1B_{2u}$	3.00	3.01	3.49	4.73	4.02	3.04	3.1

[a] Ref. [2].   [b] Ref. [32].

Table 6

Statistical analysis of calculated excitation energies of N_2, formaldehyde, ethylene and pyridine compared to the experimental values. The analysis is carried out for states below α-IP, respectively, as described in the text

| | Deviation from experiment (eV) | | | | |
	S-VWN	B-P	B3LYP	SCI	RPA
$\alpha = 0.5$ (7 states)					
mean dev.	−0.15	−0.29	−0.25	0.05	−0.77
mean abs. dev.	0.36	0.29	0.30	0.88	1.65
rms dev.	0.38	0.32	0.36	1.00	2.34
max. dev.	0.49	0.45	0.71	1.57	4.29
$\alpha = 0.6$ (15 states)					
mean dev.	−0.27	−0.41	−0.31	0.12	−0.64
mean abs. dev.	0.43	0.45	0.39	0.91	1.57
rms dev.	0.54	0.53	0.46	1.03	2.15
max. dev.	1.22	1.09	0.91	1.57	4.29
$\alpha = 1.0$ (31 states)					
mean dev.	−0.45	−0.53	−0.44	0.09	−0.39
mean abs. dev.	0.53	0.55	0.49	0.76	1.11
rms dev.	0.65	0.65	0.54	0.94	1.64
max. dev.	1.36	1.38	0.91	1.57	4.29

instability of the closed shell HF wavefunction at the experimental structure of N_2. This can clearly be seen by looking at the RPA value for this state which is in error by more than 4 eV. As we showed in a previous paper [18], the instability problem is much less severe in DFT theory. Therefore pure TDDFT should partially rectify the instability problems and our results confirm this. The overall performance of the TDDFT approach for N_2 is encouraging since the rms deviation from experimental values is reduced by a factor of five compared to RPA and by a factor of two compared to SCI.

In contrast to the situation for N_2, the excitation spectrum of ethylene is dominated by Rydberg states. Only the triplet B_{1u} state is dominantly of valence character. For this state again the problem connected to a near triplet instability occurs, making the RPA value for the excitation energy useless whereas the non-hybrid TDDFT values agree well with experiment. For ethylene the SCI method yields the best rms deviation followed by S-VWN and B-P. In view of the relatively poor performance of SCI for the other molecules under consideration, the good values in this case indicate a fortuitous error cancellation. When we exclude the instability problem case, the rms deviation of the RPA method becomes 0.167 eV and thus the HF based methods seem to work better for ethylene than TDDFT. As nearly all excitation energies are relatively high in this case (compared to the ionization potential (IP) of the molecule) this might indicate deficiencies of the adiabatic approximation for the time dependent exchange correlation functional.

Our examples for excitations of the formaldehyde molecule contain states with dominantly valence and Rydberg character. The performance of the non-hybrid TDDFT method is slightly better than SCI in this case and markedly better than RPA. Again the statistics for the latter method is affected by the near triplet instability in A_1. If this state is excluded from the statistics the rms deviation for RPA becomes 0.9 eV and thus comparable to the one for TDDFT. For formaldehyde the best agreement with experiment is obtained for the hybrid functional B3LYP.

For the pyridine molecule all the excitations we considered show dominant valence character. As for formaldehyde the pure TDDFT results are slightly better than those of the HF-based methods, particularly for the lowest excitation energies. Again the hybrid functional B3LYP yields by far the best results.

To investigate the influence of the adiabatic approximation for the exchange correlation functional on our results we tried to discriminate between lower and higher energy excitations. As a criterion we used the molecular IP. In Table 6 we show a statistical analysis in which we included those excitation energies of N_2, formaldehyde, ethylene and pyridine with an experimental value smaller than αIP.

Going from $\alpha = 0.5$ to $\alpha = 1.0$ the rms deviation of the TDDFT results for all functionals increases by a factor of two whereas the rms deviation of the SCI results remains basically unaffected. The rms deviation for the RPA results even decreases for higher α which is due to the decreasing weight of the instability problem cases mentioned above. Excluding the $^3A_1$ state of formaldehyde, the $^3B_{1u}$ of ethylene and the $^3\Delta_u$ and $^3\Sigma_u^+$ states of N_2 from our analysis, we find rms deviations of 0.78 eV ($\alpha = 0.5$), 0.84 eV ($\alpha = 0.6$) and 0.91 eV ($\alpha = 1.0$) for the RPA method. These values are slightly better but comparable to those obtained with SCI. Even though our results are far from being statistically significant since our data base is too small they seem to indicate the necessity of going beyond the adiabatic approximation for a further improvement of the method especially for high-lying states.

The correct ordering of excited states is, of course, of prime importance for a computational procedure. The B3LYP functional is very satisfactory in this respect since there is only one noticeable deviation from experiment: the $^1B_2$ ($\pi \rightarrow \pi^*$) state of pyridine is predicted 0.4 eV above the $^1A_2$ ($n \rightarrow \pi^*$) state, whereas it should be 0.4 eV below. B3LYP likewise gives reasonable singlet–triplet separations of states comparable in excitation type. Computed singlet–triplet separations differ from experiment by typically 0.2 eV, the largest discrepancy of 0.4 eV occurs for the $^{1,3}\Pi_g$ states of N_2.

As an example of a larger molecule we treated porphin. Its electronic excitation spectrum is characterized by various low-lying states of clear valence type. Since the static approximation to TDDFT appears to work best under these circumstances, satisfactory results could be expected. This is in fact the case: the computed low-lying dipole allowed electronic states $^1B_{1u}$ and $^1B_{2u}$ show deviations of only 0.2 eV from experiment for all TDDFT calculations. This is a considerable improvement over RPA and SCI which show maximum errors of 1 eV and more. The TDDFT results are in fact almost comparable in accuracy to the elaborate CAS-PT2 results of Ref. [2]. This conclusion should not be affected by the fact that a relatively small SVP basis was employed. A basis set extension, e.g. to the Sadlej basis, was found to change the energy of the low-lying excitations by less than 0.1 eV in exploratory calculations on pyridine.

4. Conclusions

The analysis presented in Table 6 shows that the TDDFT results for excitations with an energy less than half the molecular IP are clearly superior to the results obtained by the HF-based methods. The rms deviation from experiment is only about one third of the SCI value and much better than the RPA result. As previously discussed, the poor performance of the RPA method is partly due to the closed shell HF instability problem which is much less pronounced within DFT. Comparing the TDDFT results among each other, it can be seen that the gradient corrected functionals lead to slightly better results than S-VWN.

When all states are considered ($\alpha = 1$) the advantage of TDDFT over SCI or SCF-RPA becomes smaller but is still significant. It seems worthwhile to investigate whether going beyond the adiabatic approximation leads to a further improvement. In contrast to the HF-based methods, all TDDFT results show only small deviations between mean, mean absolute and rms deviations from experiment. This indicates a relatively regular behavior of the predicted TDDFT excitation energies which are typically 0.4 eV too low.

Looking at the overall performance for the molecules under consideration, the hybrid TDDFT approach using the B3LYP functional leads to the best results with a rms deviation of about 0.5 eV. This is underlined by the maximum deviation of the B3LYP results which at 0.9 eV is by far the smallest of all methods considered.

Acknowledgement

Appendix. Explicit expressions for the matrices M^p and L^p

For a functional $E_{xc}[\rho]$ of the form

$$E_{xc} = \int d^3r \, f(\rho_\alpha, \rho_\beta, \gamma_{\alpha\alpha}, \gamma_{\beta\beta}, \gamma_{\alpha\beta}), \tag{22}$$

with

$$\gamma_{\sigma\sigma'} = \nabla\rho_\sigma \nabla\rho_{\sigma'}, \tag{23}$$

the matrices M^p and L^p ($p =$ s, t) are given by

$$
\begin{aligned}
M^s_{ia,jb} = {}& 2\int d^3r \, d^3r' \, \phi_i(r)\phi_a(r) \frac{1}{|r-r'|} \phi_j(r')\phi_b(r') \\
&+ \int d^3r \, \nabla(\phi_i\phi_a)\nabla(\phi_j\phi_b)\left(2\frac{\partial f}{\partial\gamma_{\alpha\alpha}} + \frac{\partial f}{\partial\gamma_{\alpha\beta}}\right) + \int d^3r \, \phi_i\phi_a\phi_j\phi_b\left(\frac{\partial^2 f}{\partial\rho_\alpha^2} + \frac{\partial^2 f}{\partial\rho_\alpha\partial\rho_\beta}\right) \\
&+ \int d^3r \, \nabla\rho\nabla(\phi_i\phi_a)\cdot\nabla\rho\nabla(\phi_j\phi_b)\left(\frac{\partial^2 f}{\partial\gamma_{\alpha\alpha}^2} + \frac{1}{2}\frac{\partial^2 f}{\partial\gamma_{\alpha\beta}^2} + 2\frac{\partial^2 f}{\partial\gamma_{\alpha\alpha}\partial\gamma_{\alpha\beta}} + \frac{\partial^2 f}{\partial\gamma_{\alpha\alpha}\partial\gamma_{\beta\beta}}\right) \\
&+ \int d^3r \, \{\phi_i\phi_a\nabla\rho\nabla(\phi_j\phi_b) + \phi_j\phi_b\nabla\rho\nabla(\phi_i\phi_a)\}\left(\frac{\partial^2 f}{\partial\rho_\alpha\partial\gamma_{\alpha\alpha}} + \frac{\partial^2 f}{\partial\rho_\alpha\partial\gamma_{\beta\beta}} + \frac{\partial^2 f}{\partial\rho_\alpha\partial\gamma_{\alpha\beta}}\right),
\end{aligned} \tag{24}
$$

$$
\begin{aligned}
M^t_{ia,jb} = {}& \int d^3r \, \nabla(\phi_i\phi_a)\nabla(\phi_j\phi_b)\left(2\frac{\partial f}{\partial\gamma_{\alpha\alpha}} - \frac{\partial f}{\partial\gamma_{\alpha\beta}}\right) + \int d^3r \, \phi_i\phi_a\phi_j\phi_b\left(\frac{\partial^2 f}{\partial\rho_\alpha^2} - \frac{\partial^2 f}{\partial\rho_\alpha\partial\rho_\beta}\right) \\
&+ \int d^3r \, \nabla\rho\nabla(\phi_i\phi_a)\cdot\nabla\rho\nabla(\phi_j\phi_b)\left(\frac{\partial^2 f}{\partial\gamma_{\alpha\alpha}^2} - \frac{\partial^2 f}{\partial\gamma_{\alpha\alpha}\partial\gamma_{\beta\beta}}\right) \\
&+ \int d^3r \, \{\phi_i\phi_a\nabla\rho\nabla(\phi_j\phi_b) + \phi_j\phi_b\nabla\rho\nabla(\phi_i\phi_a)\}\left(\frac{\partial^2 f}{\partial\rho_\alpha\partial\gamma_{\alpha\alpha}} - \frac{\partial^2 f}{\partial\rho_\alpha\partial\gamma_{\beta\beta}}\right),
\end{aligned} \tag{25}
$$

$$L^p_{ia,jb} = \delta_{ij}\delta_{ab}(\epsilon_a - \epsilon_i) + M^p_{ia,jb}, \tag{26}$$

where the orbitals ϕ_k are assumed to be real. For the hybrid functionals the matrices M^p and L^p were obtained by scaling the expressions given above and adding the appropriately scaled exchange part from the corresponding RPA matrices (for the latter see e.g. Ref. [15]).

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