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Accurate excitation energies from time-dependent density functional theory: Assessing the PBE0 model

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We analyze the performance of a density functional model obtained by combining the Perdew–Burke–Erzenrhof (PBE) generalized gradient functional with a predetermined amount of exact exchange for predicting vertical electronic excitation energies within a time-dependent approach. Four molecules, namely, CO, H_2CO, $(CH_3)_2CO$, and C_2H_4, have been chosen as benchmark cases. Our results show that this model (PBE0) provides accurate excitations both to valence and Rydberg states. Furthermore, the results are numerically close to those obtained using asymptotically correct exchange-correlation functionals. The performance of the PBE0 model for predicting excitation energies in larger molecules is assessed for benzene, pyridine, and naphthalene. Here, the PBE0 model provides results which are in fairly good agreement with experimental data and of similar quality to those obtained by more sophisticated (and time-consuming) post-Hartree–Fock methods. © *1999 American Institute of Physics.* [S0021-9606(99)30531-6]

I. INTRODUCTION

A quantitative understanding of molecular electronic excited states is important in many domains, including spectroscopy, photochemistry, and the design of optical materials. The prediction or interpretation of the discrete part of the spectrum is a demanding task for theoretical methods, especially for medium and large size molecules of chemical interest. Thus, an inexpensive yet accurate method for calculating vertical excitation energies would be very useful.

Density Functional Theory (DFT)[1] has been remarkably successful at providing a means for computing a variety of ground state properties with an accuracy which rivals that of post-Hartree–Fock (HF) methods. Indeed, the accuracy of current DFT models is at least comparable to the results obtained by low-order many body perturbation techniques, such as the second order Møller–Plesset (MP2) approach.[2,3] Since DFT methods rectify many problems of the HF approximation at a comparable computational cost, there is currently great interest in extending the DFT approach to excited electronic states. In this context, the Time-Dependent (TD) generalization of the DFT theory (TDDFT) offers a rigorous route to the calculation of the dynamic response of the charge density.[4,5] Combining this with linear response theory allows the calculation of vertical electronic excitation spectra.[6–9]

A number of papers[6–12] have shown already that the local spin density approximation (LDA) provides results for low excitation energies usually superior to the those obtained by Time-Dependent HF methods (TDHF),[13] or the Configuration Interaction with Singles excitations (CIS) approach.[14]

In addition, given that the TDHF scheme can be derived along the same lines as TDDFT, hybrid HF/DFT methods have also been proposed for the calculation of excitation energies.[6,8] Tests have shown that the B3LYP functional represents a further improvement over conventional DFT methods.[6,8,10] However, vertical excitation energies to Rydberg states are of poor quality compared to valence states.[7] These shortcomings have been traced to an unsatisfactory description of the virtual Kohn–Sham (KS) orbitals and eigenvalues, which arises from the asymptotically incorrect behavior of most current functionals.[7,9] As a matter of fact, significant improvements in the description of high-energy transitions have been obtained by using asymptotically corrected DFT potentials[7,16] or by adding the HF potential to the DFT one at long range.[9] All these efforts point out that, like in ground-state computations, the domain of applicability of TDDFT rests on the development and validation of suitable functionals.

A number of functionals based on the generalized gradient approximation (GGA) have been developed in the last few years and are being incorporated in several computer codes (see, for instance, Refs. 15, 17–30). Fitting parameters to some set of experimental data and the fulfillment of physical constraints are common approaches to developing new functionals. Of particular importance to this paper is the PBE functional[22] which contains no parameters fitted to experimental data. PBE generally provides results which are at least comparable to those obtained with more empirical functionals.[31–34] Casting the PBE functional in a particular hybrid model,[26,35,36] where a predefined amount of HF exchange is added self-consistently to the DFT contribution yields an even more accurate functional.[37–39] Preliminary tests on a limited set of molecules[37] have shown that, using this hybrid model, vertical excitation energies are remark-

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ably close to experimental values, at least for transitions involving valence electrons.

In order to assess the performance of this functional, we study in this paper a larger set of molecules and excitations. To this end, we have focused our attention on some test cases which have become a standard set to test new TDDFT approaches.[6–10] Next, we have considered some more chemically interesting systems, like benzene and pyridine. Finally, we present results for naphthalene to demonstrate the feasibility of obtaining excitation energies for large systems of current chemical interest.

II. COMPUTATIONAL DETAILS

Time-dependent DFT provides a formally rigorous extension of the Hohenberg–Kohn–Sham formulation, which is time independent, to the situation where a system, initially in its ground stationary state, is subject to a time-dependent perturbation modifying its external potential, ν.[4] A stationary action principle may be derived, analogous to the minimum energy principle of Hohenberg–Kohn theory, and this can be used to derive the time-dependent KS equations.[4] Since the dynamic polarizability describes the response of the dipole moment to a time-dependent electric field, it may be calculated from the response of the charge density obtained from TDDFT. This allows the determination of the electronic excitation spectrum in the usual dipole approximation, because the poles of the dynamic polarizability determine the excitation energies.[7] Since our methodology has been presented in detail elsewhere,[8] we do not give here any further details. Hybrid HF/DFT methods are rooted in the adiabatic connection formula.[40] Starting from this formula, several hybrid schemes have been proposed.

The most widely used models include three empirical parameters to determine the mixing of HF and DFT exchange, and correlation.[41] More recently, Becke has suggested[42] that just one coefficient is sufficient to rule the HF/DFT exchange ratio. These methods are quite successful[43,44] and it has been shown that nonempirical hybrid schemes employing a system- and property-dependent mixing coefficient can be approximated quite accurately.[45]

Perdew and co-workers have also proposed that based on fourth order perturbation theory, the optimum value of the mixing coefficient should be set to $1/4$.[46] The resulting exchange-correlation functionals can be expressed as

$$E_{xc} = E_x^{GGA} + \frac{1}{4}(E_{xc}^{HF} - E_x^{GGA}). \tag{1}$$

Remarkable features of this family of functionals are that they do not have additional parameters with respect to their GGA component and that some of them deliver very good numerical results.[26,36] In particular the PBE0 variant is obtained inserting the PBE GGA model in Eq. (1). We have recently added[37,38] both PBE and PBE0 functionals to the standard DFT approaches available in the GAUSSIAN98 package.[47,48] In some cases, computations have also been carried out using the Becke exchange with the correlation functional developed by Lee, Yang, and Parr, either in a pure DFT (BLYP) or hybrid HF/DFT (B3LYP) scheme.[47]

All computations in this paper have been carried out with the development version of the GAUSSIAN package.[48] Note that, in analogy with our previous implementations,[26,36] the GAUSSIAN keyword for the PBE functional is PBEPBE, whereas both PBE0 and PBE1PBE are accepted for the PBE0 model.

A number of different basis sets have been used in this study. All the ground state molecular structures have been optimized with the 6-311G(d,p) basis set,[47,49] given that previous experience showed that a polarized valence triple-ζ basis set generally provides nearly converged structural parameters by DFT methods.[50,51] Following a recent study by Wiberg et al.,[10] vertical excitation energies have been evaluated adding diffuse functions on all atoms [leading to the 6-311++G(d,p) basis]. In order to compare our computations with previous published results, the basis set developed by Sadlej[52,53] has also been used. Here, following the indications of Casida et al.,[7] we have augmented this basis set with additional diffuse functions to aid in the description of excitations to Rydberg states. The resulting basis set will be referred to as Sedlej+.

III. RESULTS

Four small, well-studied molecules, namely, carbon oxide, formaldehyde, ethylene, and acetone, have been chosen as test cases in order to evaluate the quality of PBE0 excitation energies. These molecules may also be considered as prototypes for studying the $n-\pi^*$ and $\pi-\pi^*$ transitions which are important for organic photochemistry. Furthermore, these molecules have previously been investigated in detail at the post-HF[54–64] and TDDFT[7–11] levels of theory. Next, excitation energies were computed for three aromatic molecules, namely, benzene, pyridine, and naphthalene, in order to show that TDDFT provides accurate results for valence and Rydberg states of chemically interesting systems.

A. Test cases

In Tables I–IV we report the calculated vertical excitation energies for our test cases using the PBE and PBE0 functionals. To better elucidate the performance of both models, we report also values determined using the B3LYP functional as well as those obtained by the HCTH and HCTH(AC) functionals.[9] In the same tables, the corresponding experimental values[65–68] are also presented. We do not report post-HF computations, since detailed comparisons between these results and those obtained by TDDFT approaches have been already presented in several papers (see, for instance, Refs. 7 and 9). The main conclusion is that current GGA functionals (like BLYP) provide reasonably good valence excitations energies, but fail on higher energy Rydberg excitations.[7] Significant improvements can be obtained introducing some HF exchange (like in the B3LYP model), but the Rydberg excitations still remain poor.[8]

More recently, two studies[7,9] have pointed out that significant improvements to Rydberg excitations result from functionals that have the correct $(1/r)$ asymptotic behavior. In particular, Handy and Tozer[9] have shown that mixing the HF potential with the DFT one at long range yields improved results. Their functional, HCTH(AC), gives errors of about

TABLE I. Vertical excitation energies of CO (in eV) calculated using different functionals and basis sets. The PBE and PBE0 values are calculated using the PBE0/6-311G(d,p) geometry.

State	B3LYP[a] Sadlej+	HCTH[a] Sadlej+	HCTH(AC)[a] Sadlej+	PBE Sadlej+	PBE0 6-311++G(d,p)	PBE0 Sadlej+	exp.[b]
$^1\Sigma^+$	10.49	9.58	12.07	9.88	12.01	12.12	12.40
$^1\Pi$	10.30	9.48	11.11	10.58	11.49	11.49	11.53
$^3\Pi$	10.26	9.30	10.94	9.81	11.24	10.97	11.55
$^1\Sigma^+$	10.24	9.41	11.17	10.52	11.39	11.33	11.40
$^3\Sigma^+$	10.20	9.33	10.98	9.84	10.96	10.98	11.30
$^1\Sigma^+$	9.77	8.94	10.33	9.95	10.75	10.68	10.78
$^3\Sigma^+$	9.50	8.69	9.93	9.86	10.10	9.80	10.40
$^1\Delta$	10.03	10.19	10.23	9.90	10.23	10.20	10.23
$^1\Sigma^-$	9.70	9.92	9.95	9.84	9.81	9.79	9.88
$^3\Sigma^-$	9.70	9.92	9.95	9.35	9.81	9.69	9.88
$^3\Delta$	8.62	8.94	8.96	8.76	8.66	8.63	9.36
$^1\Pi$	8.40	8.31	8.38	8.25	8.45	8.45	8.51
$^3\Sigma^+$	7.90	7.91	7.93	8.11	7.87	7.86	8.51
$^3\Pi$	5.84	5.90	5.91	5.74	5.74	5.73	6.32
MAE	0.76	1.09	0.32	0.77	0.26	0.32	

[a]Reference 9.
[b]Calculated in Ref. 54 from data of Ref. 62.

0.2–0.3 eV for all the test cases considered. It is then natural that this functional, and its parent HCTH functional, would be our reference point. We stress that our tests are particularly stringent because both valence and Rydberg excitations have been considered in all our comparisons. In particular, for the carbonyl compounds, H_2CO and $(CH_3)_2CO$, two low-lying singlet and triplet states correspond to $n-\pi^*$ and $\pi-\pi^*$ excitations, while the remaining transitions involve Rydberg states. In CO instead, the lowest 7 transitions (singlets and triplets) are either $\sigma-\pi^*$ or $\pi-\pi^*$, while the highest are all excitations to Rydberg states. Finally, the low-lying excitations in acetylene all originate from a π orbital (b_{3u} symmetry), but only two lead to π^* orbitals, all the other involving, instead, Rydberg states.

We begin our discussion of results with the analysis of the PBE functional whose Mean Absolute Errors (MAE) are 0.77, 1.06, 0.35, and 0.40 eV for CO, H_2CO, $(CH_3)_2CO$, and C_2H_4, respectively. These errors are always smaller that

those obtained with the HCTH functional. Furthermore, the PBE results are numerically close, and sometimes better, than those obtained using the functional developed by van Leeuwen and Baerends, which has the correct asymptotic behavior.[7,15] A detailed comparison with the latter functional was not possible because these authors only reported a few of the electronic transitions considered here. In summary, the PBE functional gives results which are better than those provided by other GGA models and are often close to those provided by the B3LYP approach.

Turning now our discussion to the hybrid PBE0 model, the MAE for CO, H_2CO, $(CH_3)_2CO$, and C_2H_4, are 0.32, 0.30, 0.19, and 0.21 eV, respectively. These errors are significantly smaller than those found with the B3LYP approach, and close to those of the HCTH(AC) functional. This agreement is particularly remarkable because HCTH(AC) was designed with excitation energies in mind, whereas PBE0 contains no adjustable parameters. Furthermore, the

TABLE II. Vertical excitation energies of H_2CO (in eV) calculated using different functionals and basis sets. The PBE and PBE0 values are calculated using the PBE0/6-311G(d,p) geometry.

State	B3LYP[a] Sadlej+	HCTH[a] Sadlej+	HCTH(AC)[a] Sadlej+	PBE Sadlej+	PBE0 6-311++G(d,p)	PBE0 Sadlej+	exp.[b]
$^1A_2$	7.94	7.11	9.29	7.16	9.45	9.43	9.22
$^1A_2$	7.34	6.54	8.12	7.00	8.15	8.14	8.38
$^1B_1$	9.03	8.98	8.99	8.90	8.55	8.57	8.68
$^1B_2$	7.13	6.38	7.67	6.30	7.85	7.69	8.12
$^3B_2$	7.06	6.30	7.53	6.92	7.65	7.59	7.96
$^1A_1$	7.10	6.33	7.87	6.28	7.76	7.37	7.97
$^3A_1$	7.06	6.19	7.74	6.64	7.53	7.53	7.79
$^3B_2$	6.38	5.69	6.77	5.68	6.53	6.45	7.09
$^1B_2$	6.27	5.56	6.63	5.73	6.78	6.66	6.83
$^3A_1$	5.46	5.81	5.82	5.89	5.36	5.35	5.53
$^1A_2$	3.92	3.92	3.93	3.82	3.98	3.96	3.94
$^3A_2$	3.19	3.27	3.28	3.13	3.20	3.18	3.50
MAE	0.65	1.17	0.23	1.06	0.23	0.30	

[a]Reference 9.
[b]References 63 and 64.

TABLE III. Vertical excitation energies of C_2H_4 (in eV) calculated using different functionals and basis sets. The PBE and PBE0 values are calculated using the PBE0/6-311G(d,p) geometry.

State	B3LYP[a] Sadlej+	HCTH[a] Sadlej+	HCTH(AC)[a] Sadlej+	PBE Sadlej+	PBE0 6-311++G(d,p)	PBE0 Sadlej+	exp.[b]
$^1B_{1u}$	8.14	7.82	9.32	8.85	9.30	9.33	9.33
$^1B_{2u}$	7.87	7.37	9.04	8.78	9.09	9.02	9.05
$^1B_{3u}$	7.75	7.29	8.95	8.26	8.82	8.76	8.90
$^1B_{3u}$	7.36	6.86	8.70	8.25	8.69	8.65	8.62
$^3B_{3u}$	7.34	6.86	8.64	8.65	8.66	8.55	8.57
^1A_g	7.41	6.94	8.33	8.11	8.08	8.04	8.28
^3A_g	7.33	6.79	8.15	8.04	8.34	8.08	8.15
$^1B_{1u}$	7.36	7.18	7.61	7.46	7.60	7.58	7.66
$^1B_{2g}$	7.09	6.68	7.77	7.03	7.62	7.52	8.00
$^1B_{1g}$	7.08	6.69	7.78	7.08	7.59	7.51	7.80
$^3B_{1g}$	7.05	6.65	7.76	7.06	7.42	7.36	7.79
$^1B_{3u}$	6.57	6.24	7.16	6.52	6.99	6.93	7.11
$^3B_{3u}$	6.50	6.19	7.10	6.48	6.85	6.79	6.98
$^3B_{1u}$	4.07	4.32	4.33	4.34	3.94	3.92	4.36
MAE	0.83	1.18	0.06	0.40	0.17	0.19	

[a]Reference 9.
[b]Reference 62.

performance of PBE0 for singlet and triplet states was comparable in all test cases. The drastic improvement observed in going from PBE to PBE0 emphasizes how HF exchange does not significantly affect the valence excitations, but it strongly influences excitations to higher Rydberg states.

Data presented in Tables I–IV for the PBE0 functional were obtained using both the large Sadlej+ basis set and the smaller 6-311++G(d,p). The agreement between the two data sets is remarkable, and indicates that the latter basis is, at least for the molecules under consideration, sufficiently converged for excitation energies even to Rydberg states. We have also carried out some calculations with the standard 6-311G(d,p) basis set and the results, not reported here, show that diffuse functions are necessary to obtain accurate excitations to Rydberg states. Additional polarization functions were found to have little effect.[10] So, the 6-311++G(d,p) basis set can be considered as an excellent compromise between size and accuracy.

B. Aromatic systems

Ab-initio calculations of excitation energies for medium size molecules are not abundant in the literature because of the computational cost involved. Nevertheless, different theoretical studies have been carried out for the electronic spectrum of benzene.[12,69–72] The principal excitations of benzene which are of interest are those involving the degenerate π HOMO and the degenerate π^* LUMO, other $\pi \rightarrow \pi^*$ valence excitations, and excitations from the HOMO to the Rydberg orbitals, namely, $3s$, $3p$, and $3d$. In total, 16 singlet and 13 triplet states have been considered in the present study, with experimental excitation energies ranging between 3.6 to 7.6 eV.

The results are reported in Tables V and VI, together with experimental (from Ref. 70) and CASPT2[69] results. There are other post-HF studies in the literature, based on a multi-reference perturbation approach[72] and on the second order

TABLE IV. Vertical excitation energies of $(CH_3)_2CO$ (in eV) calculated using different functionals and basis sets. The PBE and PBE0 values are calculated using the PBE0/6-311G(d,p) geometry.

State	B3LYP 6-311++G(d,p)	PBE 6-311++G(d,p)	PBE0 6-311++G(d,p)	PBE0 Sadlej+	exp.[a]
$^1A_2$	7.47	7.56	7.92	8.18	8.09
$^3A_2$	6.95	7.80	8.15	8.07	7.90
$^1B_2$	7.21	6.41	7.45	7.52	7.49
$^1A_1$	6.83	5.94	7.06	7.04	7.41
$^1A_2$	6.96	6.15	7.21	7.18	7.36
$^1B_2$	6.11	5.02	6.11	6.08	6.36
$^3A_2$	5.80	6.11	6.03	6.00	6.26
$^3A_1$	5.84	5.79	5.59	5.59	5.88
$^1A_2$	4.44	4.28	4.47	4.46	4.43
$^3A_2$	3.86	3.66	3.79	3.78	4.18
MAE	0.39	0.67	0.22	0.21	

[a]Reference 65.

TABLE V. Vertical singlet excitation energies of C_6H_6 (in eV) calculated using different functionals and basis sets. All calculations were performed in D_{6h} symmetry with $r_{CC}=1.392$ Å and $r_{CH}=1.086$ Å.

State	CASPT2[a]	B3LYP 6-311++G(d,p)	HCTH(AC)[b] 6-31G(d)[c]	HCTH(AC)[b] TZ2P[c]	PBE 6-311++G(d,p)	PBE0 6-311++G(d,p)	Sadlej+	exp.[d]
			Valence $\pi\rightarrow\pi^*$					
$1\ ^1B_{2u}$	4.84	5.39	5.44	5.28	5.26	5.50	5.48	4.90
$1\ ^1B_{1u}$	6.30	6.05	6.24	6.02	5.89	6.17	6.16	6.20
$1\ ^1E_{1u}$	7.03	6.93	7.00	6.94	6.88	6.94	6.92	6.94
			Rydberg $\pi\rightarrow\pi^*$					
$2\ ^1E_{1u}$	7.16	7.21	7.34	7.24	7.07	7.18	7.14	7.41
$1\ ^1E_{2g}$	7.77	7.52	7.66	7.76	7.20	7.71	7.65	7.81
$2\ ^1A_{1g}$	7.74	7.55	7.63	7.78	7.22	7.73	7.67	7.81(?)
$1\ ^1A_{1g}$	7.81	7.58	7.63	7.80	7.23	7.75	7.70	7.81
			Rydberg $\pi\rightarrow\sigma^*$					
$1\ ^1E_{1g}$	6.38	6.06	6.15	6.24	6.00	6.37	6.32	6.33
$1\ ^1A_{2u}$	6.86	6.55	6.81	6.92	6.44	6.89	6.82	6.93
$1\ ^1E_{2u}$	6.91	6.58	6.79	6.90	6.46	6.93	6.86	6.95
$1\ ^1A_{1u}$	6.99	6.93	6.81	6.91	6.86	7.00	6.92	
$2\ ^1E_{1g}$	7.57	7.44	7.41	7.51	7.17	7.59	7.49	7.54
$1\ ^1B_{2g}$	7.58	7.44	7.41	7.52	7.13	7.59	7.49	7.46
$1\ ^1B_{1g}$	7.58	7.43	7.39	7.50	7.12	7.58	7.48	7.46
$3\ ^1E_{1g}$	7.57	7.43	7.38	7.45	7.11	7.44	7.43	
MAE	0.08	0.29	0.19	0.12	0.40	0.14	0.15	

[a]Reference 69.
[b]Reference 12.
[c]Including a double-ζ set of diffuse functions.
[d]From Ref. 70.

polarization propagator approximation (SOPPA).[70] Here, we shall not comment on these *ab-initio* studies except for the CASPT2 results which we deem as the most accurate.

Handy and Tozer[12] have recently presented a detailed TDDFT study on benzene using the HCTH functional, both in the pure and in the asymptotically corrected HCTH(AC) form. They showed that the HCTH(AC) functional outperforms standard functionals including B3LYP, for predicting electronic transitions, and that it provides results of accuracy similar to that obtained with the CASPT2 method. For comparison purposes, we include the HCTH(AC) results in Tables V and VI, and computed excitation energies using the

TABLE VI. Vertical triplet excitation energies of C_6H_6 (in eV) calculated using different functionals and basis sets. All calculations were performed in D_{6h} symmetry with $r_{CC}=1.392$ Å and $r_{CH}=1.086$ Å.

State	CASPT2[a]	B3LYP 6-311++G(d,p)	HCTH(AC)[b] 6-31G(d)[c]	HCTH(AC)[b] TZ2P[c]	PBE 6-311++G(d,p)	PBE0 6-311++G(d,p)	Sadlej+	exp.[d]
			Valence $\pi\rightarrow\pi^*$					
$1\ ^3B_{1u}$	3.89	3.82	4.11	4.02	4.06	3.64	3.63	3.94
$1\ ^3E_{1u}$	4.49	4.70	4.78	4.66	4.65	4.73	4.71	4.76
$1\ ^3B_{2u}$	5.49	5.05	5.15	4.98	5.11	5.13	5.08	5.60
$1\ ^3E_{2g}$	7.12	7.18	7.30	7.20	7.23	7.39	7.34	7.24
			Rydberg $\pi\rightarrow\pi^*$					
$2\ ^3E_{1u}$	6.98	6.66	7.01	7.13	7.05	7.00	6.92	
$2\ ^3E_{2g}$	7.55	7.33	7.60	7.74	7.15	7.62	7.61	
			Rydberg $\pi\rightarrow\sigma^*$					
$1\ ^3E_{1g}$	6.34	6.02	6.11	6.21	6.38	6.31	6.26	
$1\ ^3A_{2u}$	6.80	6.51	6.72	6.85	6.70	6.80	6.74	
$1\ ^3E_{2u}$	6.90	6.58	6.76	6.88	6.72	6.91	6.84	
$1\ ^3A_{1u}$	7.00	6.67	6.81	6.91	6.78	6.91	6.84	
$2\ ^3E_{1g}$	7.57	7.21	7.37	7.48	7.10	7.43	7.40	
$1\ ^3B_{1g}$	7.53	7.19	7.35	7.46	7.05	7.39	7.39	
$1\ ^3B_{2g}$	7.53	7.33	7.38	7.50	7.12	7.44	7.44	
$1\ ^3E_{1g}$	7.56	7.33	7.34	7.40	7.11	7.40	7.39	
MAE[e]		0.26	0.19	0.13	0.28	0.14	0.16	

[a]Reference 69.
[b]Reference 12.
[c]Including a double-ζ set of diffuse functions.
[d]From Ref. 70.
[e]DFT MAE's are calculated with respect to CASPT2 results.

TABLE VII. Singlet vertical excitation energies of pyridine (in eV) calculated using different functionals and basis sets. The PBE and PBE0 values are calculated using the PBE0/6-311G(d,p) geometry.

State	CASPT2[a]	B3LYP 6-311++G(d,p)	PBE 6-311++G(d,p)	PBE0 6-311++G(d,p)	Sadlej+	exp.[b]
			Valence $\pi \rightarrow \pi^*$			
$1\,^1B_2$	4.84	5.54	5.42	5.63	5.61	4.99
$1\,^1A_1$	6.42	6.24	6.10	6.42	6.39	6.38
$3\,^1A_1$	7.23	6.90	6.27	7.21	7.12	7.22
$3\,^1B_2$	7.48	7.25	7.11	7.37	7.32	
$5\,^1A_1$	7.96	7.70	7.26	7.98	7.84	
			Valence $n \rightarrow \pi^*$			
$1\,^1B_1$	4.91	4.80	4.38	4.88	4.85	4.59
$1\,^1A_2$	5.17	5.09	4.45	5.20	5.19	5.43
			Rydberg $\sigma \rightarrow \pi^*$			
$2\,^1A_1$	6.70	6.32	5.37	6.56	6.50	6.28
$2\,^1A_2$	6.75	6.42	6.17	6.69	6.62	
$2\,^1B_2$	7.21	6.74	6.75	7.06	6.99	
$2\,^1B_1$	7.25	6.93	6.71	7.21	7.13	6.93
$3\,^1B_1$	7.39	7.08	6.78	7.38	7.31	
$4\,^1A_1$	7.35	7.32	6.86	7.44	7.35	
$3\,^1A_2$	7.52	7.18	6.93	7.46	7.39	
$4\,^1A_2$	7.98	7.64	7.09	7.73	7.60	
$4\,^1B_2$	7.41	7.45	7.09	7.76	7.67	
$5\,^1A_2$	8.03	7.67	7.33	7.99	7.68	
$4\,^1B_1$	7.45	7.73	7.37	8.01	7.89	
$5\,^1B_1$	8.03	7.83	7.37	8.11	7.94	
$6\,^1B_1$	8.14	7.84	7.47	8.15	7.97	
MAE[c]		0.27	0.93	0.14	0.19	

[a]Reference 75.
[b]Reference 76.
[c]DFT MAE's are calculated with respect to CASPT2 results.

same geometry of Ref. 12 ($r_{CC} = 1.392$ Å and $r_{CH} = 1.086$ Å), which is, anyway, very close to that optimized at the PBE0/6-311G(d,p) level ($r_{CC} = 1.390$ Å and $r_{CH} = 1.085$ Å).

Our calculations are in good agreement with the HCTH(AC) results. In particular, the MAE obtained from the PBE0/Sadlej+ computations for the singlet states (0.15 eV), is close to the MAE obtained by the HCTH(AC) functional using the TZ2P basis set (0.12 eV), and less than twice the CASPT2 error of 0.08 eV. A similar trend is found for the triplet excitations, indicating that both singlet and triplet states are well-reproduced by PBE0.

The PBE0 predictions do not show a systematic error pattern: ionic and covalent states are handled in a similar manner. For instance the $^3B_{2u}$ state is ionic and the $^1B_{2u}$ is covalent, but both are predicted with a significant error. In contrast other ionic states (e.g., $^1B_{1u}$) have very low errors. It must also be noted that the B3LYP results are more accurate for benzene than for the test cases; the MAE is 0.29 and 0.26 eV, for the singlet and triplet manifolds, respectively.

We next analyze the different excitations in some detail. The singlet excitations can be divided, according to previous work,[69,70] into three classes (see Table V). The valence $\pi - \pi^*$ excitations are given to within 0.19 eV of experiment, a deviation which is higher than that provided by CASPT2 (0.08 eV),[69] but close to the SOPPA result (0.21 eV).[72] However, we must observe that the DFT prediction for the $^1B_{2u}$ state is very poor (too high by 0.58 eV at the PBE0/Sadlej+ level). This transition is incorrectly predicted also

by the other TDDFT approaches (see Table V) and also within the TDHF method (5.82 eV),[69] thus suggesting the presence of more subtle effects.

Satisfactory accuracy has been obtained for all the $\pi - \pi^*$ Rydberg excitations, the MAE being 0.17 eV, at the PBE0/Sadlej+ level. A worse agreement with experiment is obtained for the $^1E_{1u}$ transition (0.2 eV too low), but in this case PBE0 and CASPT2 results are in remarkable agreement (7.14 vs 7.16 eV).

Finally, the higher Rydberg $\pi - \sigma^*$ excitations are well reproduced at the PBE0/Sadlej+ level, with a MAE of only 0.05 eV and a maximum error of 0.11 eV. Here the accuracy of the PBE0 approach is comparable to that of CASPT2 and significantly better than that of TDHF and SOPPA.

The lowest 13 triplet excitation energies of benzene are listed in Table VI. Since experimental values are available for the valence excitations only, we use CASPT2 results as references. We found that, once again, the PBE0 predictions are close to the HCTH(AC) data, both methods showing almost the same error (0.14 and 0.13 eV, respectively). Here the maximum deviation with respect to either experimental and CASPT2 values (-0.53 eV) is found for the $^1B_{2u}$ state. We also note that for benzene the predictions using the Sadlej+ and the 6-311++G(d,p) basis sets are close to each other, both sets providing almost the same errors.

Another well studied molecule is pyridine, whose electronic spectrum has been analyzed in detail by several post-HF methods,[73–75] including CASPT2.[75] A careful experimental investigation of it has also been carried out.[76] The

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PBE0 model excitation energy   2895

TABLE VIII. Vertical triplet excitation energies of pyridine (in eV) calculated using different functionals and basis sets. The PBE and PBE0 values are calculated using the PBE0/6-311G(d,p) geometry.

State	CASPT[a]	B3LYP 6-311++G(d,p)	PBE 6-311++G(d,p)	PBE0 6-311++G(d,p)	Sadlej+	exp.[b]
			Valence $\pi \rightarrow \pi^*$			
$1\,^3A_1$	4.05	3.99	4.21	3.80	3.79	4.10
$1\,^3B_2$	4.56	4.57	4.51	4.56	4.52	4.84
$2\,^3A_1$	4.73	4.91	4.87	4.92	4.89	
$2\,^3B_2$	6.02	5.68	5.52	5.72	5.67	
$3\,^3A_1$	7.34	6.86	6.78	7.14	7.06	
$3\,^3B_2$	7.28	6.71	6.64	7.01	6.95	
			Valence $n \rightarrow \pi^*$			
$1\,^3B_1$	4.41	4.08	3.71	4.09	4.08	
$1\,^3A_2$	5.10	4.95	4.29	5.04	5.02	
MAE[c]		0.26	0.21	0.20	0.23	

[a]Reference 75.
[b]Reference 76.
[c]DFT MAE's are calculated with respect to CASPT2 results.

transitions computed by several TDDFT models are reported in Table VII and VIII. From these tables, we note a generally good agreement between PBE0 results and the few available experimental data. A more complete comparison with CASPT2 results shows a quite small average deviation (0.14 eV) between the two sets of results. In contrast, the average deviation between PBE and CASPT2 values is quite large (0.93 eV) and significantly worse than that obtained at the B3LYP level (0.27 eV). These latter results, together with those obtained for benzene, shows that the popular B3LYP approach performs relatively well for aromatic molecules, even for higher excited states.

Let us now discuss in some details the different transitions. The vacuum UV spectrum of pyridine shows three $\pi - \pi^*$ absorption bands centered at 4.99, 6.38, and 7.22 eV. The PBE0 energies for the transitions leading to $1\,^1A_1$ and $3\,^1A_1$ states (6.42 and 7.21 eV, respectively) are in good agreement with the experiments,[76] whereas a significant discrepancy has been found for the lowest transition leading to the $1\,^1B_2$ state (5.63 and 4.99 eV according to PBE0 and experiment, respectively). However, this last failure is shared by all the other TDDFT models considered in the present study (PBE and B3LYP).

The PBE0 energies for the remaining $\pi - \pi^*$ transitions are very close to the CASPT2 results. In this connection, it must be pointed out that fast post-HF methods, like CIS, fail to reproduce the experimental state ordering and the computed excitation energies are spread over a wide range.[14]

The energies and assignments of the $n - \pi^*$ valence excited states of pyridine are, unfortunately, not as well defined as those of the $\pi - \pi^*$ transitions. In any case, two transitions appear well characterized experimentally, at 4.59[77] and 5.43 eV,[78] respectively. The PBE0 approach predicts two bands centered at 4.88 and 5.20 eV, relatively far from the experimental data, but within 0.03 eV of the CASPT2 results. The large discrepancy between computed and experimental results has been attributed to the fact that only the region of the band origin is observed for the $n - \pi^*$ state in the experimental spectrum because the vertical peak is buried under the peak corresponding to the transition leading to the $1\,^1B_2$ state.[75]

The Rydberg spectrum of pyridine has been studied in detail, and a first band has been observed at 6.28 eV.[76] For symmetry reasons the lowest observed Rydberg state must belong to the A_1 representation. The second would be therefore either B_1 or possibly an A_2 state. Here, according to previous calculations, it has been assigned to the B_1 representation, so that both experimental values are overestimated by our computations. Unfortunately, no other transitions have been assigned experimentally and we must resort once again to CASPT2 results. It is indeed gratifying that PBE0 and CASPT2 values are found to be in fair agreement.

Similar trends are obtained also for the triplet excitations of pyridine (see Table VIII). In fact, the assignment of the lowest triplet states of pyridine is not well defined. The only two transitions which have been assigned with some confidence are two valence excitations centered at 4.10 and 4.84 eV.[78] The PBE0 computations correctly reproduce the experimental energy order, the $^1A_1$ state being the most stable. While the energies of both transitions are underestimated by PBE0 computations with respect to the experimental data (by 0.20 and 0.28 eV, respectively), they are close to the CASPT2 results.

In summary, our results point out that also for pyridine, the PBE0 method gives results close to CASPT2. Furthermore, as for the other molecules, the predictions using the Sadlej+ and the 6-311++G(d,p) basis set are very similar to each other. As a consequence, we will use only this latter basis set for the larger naphthalene molecule.

Much effort has been devoted to understanding the absorption spectrum of naphthalene. Although benzene is a prototype of aromatic molecules, naphthalene is more interesting for spectroscopic studies, since its lower symmetry allows transitions which are forbidden in benzene. Naphthalene is thus one of the most investigated polyacenes, both from the experimental and theoretical point of view (for a complete list of references see Ref. 72). Also, for this molecule there are comparatively few post-HF studies[70,72,79,80]

TABLE IX. Singlet excitations in naphthalene (in eV) calculated using different functionals and basis sets. The PBE and PBE0 values are calculated using the 6-311++G(d,p) basis set and the PBE0/6-311G(d,p) geometry. The Rydberg states are indicated by (R).

State	CASPT2[a]	TDHF[b]	PBE0	exp.[b]
$1\,^1B_{3u}$	4.03	5.02	4.48	4.0
$1\,^1B_{2u}$	4.56	4.80	4.58	4.70
$1\,^1A_u(R)$	5.54	5.76	5.50	5.6
$1\,^1A_g$	5.39	6.88	7.00	5.52
$1\,^1B_{1g}$	5.53	6.21	5.62	5.22
$1\,^2B_{3u}$	5.54	6.57	6.23	5.89
$1\,^1B_{2g}(R)$	5.94	6.13	5.84	
$1\,^1B_{3g}(R)$	5.98	6.20	5.84	
$2\,^1B_{2u}$	5.93	6.67	5.99	6.0
$1\,^1B_{1u}(R)$	6.03	6.45	6.29	
$2\,^1B_{1g}$	5.87	6.61	6.35	5.8
$3\,^1B_{1g}(R)$	6.08	7.14	6.93	
$2\,^1B_{2g}(R)$	6.45	6.86	6.68	
$2\,^1B_{1u}(R)$	6.50	6.73	6.44	
$2\,^1B_{3g}(R)$	6.48	6.95	6.62	
$3\,^1B_{3u}(R)$	6.58	6.86	7.23	
$3\,^1A_g(R)$	6.04	7.15	6.24	6.05
$4\,^1A_g(R)$	6.76	7.80	7.01	
MAE[c]		0.64	0.35	

[a]Reference 79.
[b]Reference 70.
[c]TDHF and PBE0 MAE's are calculated with respect to CASPT2 results.

and only the lowest transition energies have been computed using the TDDFT approach.[81]

In Tables IX and X we collect the singlet and triplet excitations. In the same table the corresponding experimental and CASPT2 results[79] are reported. With a few exceptions, the PBE0 and CASPT2 results are quite close, the PBE0 mean absolute deviation with respect to the CASPT2 ones being 0.35 eV for the singlet and 0.15 eV for the triplet states. The agreement between TDHF and CASPT2 results is definitely worse; the TDHF mean absolute deviation with respect to CASPT2 are 0.64 and 0.73 eV, for singlet and triplet states, respectively. Significant differences are found for all the ^1A_g and the $3\,^1B_{1g}$ transitions, which are overestimated by all

TABLE X. Triplet excitations in naphthalene (in eV) calculated using different functionals and basis sets. The PBE and PBE0 values are calculated using the 6-311++G(d,p) basis set and the PBE0/6-311G(d,p) geometry.

State	CASPT2[a]	TDHF b	PBE0	exp.[b]
$1\,^3B_{2u}$	3.04	instability	2.64	
$1\,^3B_{3u}$	3.84	3.67	3.99	
$1\,^3B_{1g}$	4.18	2.32	4.09	4.33
$2\,^3B_{2u}$	4.24	instability	4.31	
$2\,^3B_{3u}$	4.40	4.43	4.46	
$1\,^3A_g$	5.22	4.57	5.27	5.25
$2\,^3B_{1g}$	5.65	6.26	5.68	6.0/6.12
$3\,^3B_{1g}$	6.18	6.95	6.24	
$2\,^3A_g$	5.77	6.39	5.97	
$3\,^3A_g$	5.85	6.94	6.23	5.93
MAE[c]		0.73	0.15	

[a]Reference 79.
[b]Reference 70.
[c]DFT MAE's are calculated with respect to CASPT2 results.

TD approaches (either TDDFT and TDHF[72]) with respect to the CASPT2 data. The two lowest excitations are of B_{3u} and B_{2u} symmetry and are well described by the PBE0 approach, especially the second one which is 0.02 eV above CASPT2 and 0.12 eV below experimental data. The energies of these two transitions are significantly overestimated by other post-HF methods like SAC-CI.[80] The next PBE0 excitation leads to the Rydberg $1\,^1A_u$ state, in contrast with the CASPT2 prediction $(2A_g)$, but in agreement with SOPPA results.[72] Also in this case the error with respect to both CASPT2 and experimental data is small.

Triplet absorption spectrum of naphthalene has also been studied experimentally. It is well established that the symmetry of the lowest triplet state is $1\,^3B_{2u}$, and also the higher $3\,^3A_g$ and $2\,^3B_{1g}$ states are well characterized; unfortunately, the experimental information on the other states is rather limited. The PBE0 results show an overall good agreement with these few experimental data and with the CASPT2 results for the whole manifold of triplet states (MAE=0.15 eV). It is also noteworthy that the TDHF approach shows two instabilities for two triplet states belonging to the B_{2u} representations.

IV. DISCUSSION

The simultaneous description of valence and Rydberg excitations is a demanding task for a functional. The TDDFT approach has been found to give remarkably good results for the low-lying vertical excitations, even when LDA is used.[82] In contrast, the quality of results for higher excitations energies worsens.[6,82] This deterioration seems to be related to the onset of the ionization continuum occurring in standard DFT approaches at which energies are too low.[82] The ionization threshold for DFT methods is the negative of the highest occupied molecular orbital (HOMO) energy, $-\epsilon_{\text{HOMO}}$, which should be the exact ionization potential (IP) in the limit of the exact functional.[83] However, in current functionals HOMO electrons are generally underbound due to a too rapid asymptotic decay of the exchange correlation potential, ν_{xc}, making the ionization threshold substantially too low.[84] It has been suggested that the use of an exchange-correlation potential with the correct asymptotic behavior,

$$\lim_{r\to\infty} \nu_{\text{xc}}(r) = -\frac{1}{r}, \tag{2}$$

would improve higher excitation energies. In fact, reasonable results are obtained using the asymptotically correct potential of van Leeuwen and Baerends[15] in the SCF step, combined with the time-dependent LDA for the post-SCF step.[7] Alternatively, Handy and Tozer added a Fermi–Amaldi potential (which has the correct asymptotic behavior) to their HCTH functional in regions far from nuclei.[9] It must be pointed out, however, that in both approaches first and second derivatives of the functionals, required for geometry optimization, frequencies, and other properties, cannot be evaluated at the same level (with the same functional), thus introducing some incoherence in the computational protocol. In hybrid func-
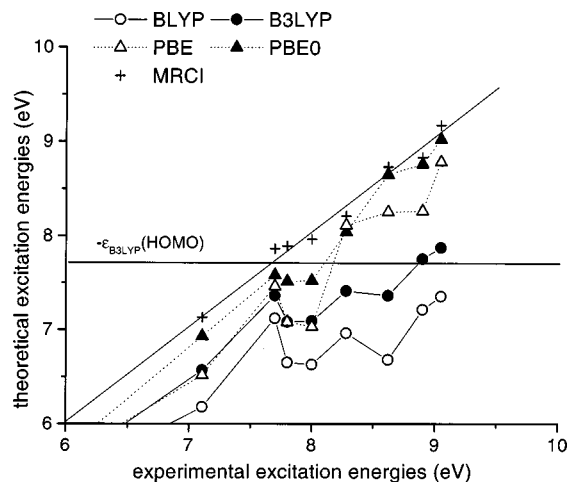
FIG. 1. The correlation plot comparing computed TD-DFT and the multi-reference configuration interaction (MRCI, from Ref. 60) results with experimental data for the vertical excitation energies of ethylene close to the HOMO energy. The TD-DFT have been calculated using the Saddlej+basis set.
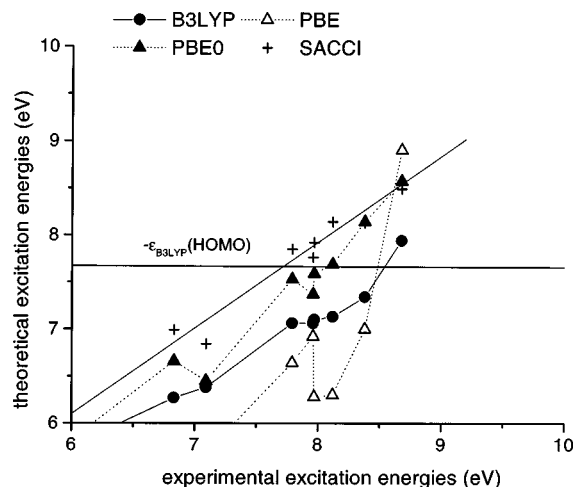

FIG. 2. The correlation plot comparing computed TD-DFT and multireference configuration interaction (SAC-CI, from Ref. 57) results with experimental data for the vertical excitation energies of formaldehyde close to the HOMO energy. The TD-DFT have been calculated using the Saddlej+basis set.

tionals, the asymptotic potential comes closer to the correct behavior, since they decay as $-a/r$, where a is some constant other than 1.[85]

The PBE potential has not the correct $1/r$ behavior.[86] Nevertheless, it provides results which are often of similar quality to those obtained with the hybrid B3LYP functional. The introduction of HF exchange, leading to the PBE0 model, allows for improvement. Furthermore, we seem to have obtained accurate results not only for low energy excitations, but also for transitions close to $-\epsilon_{HOMO}$. To better elucidate this point, in Fig. 1 we report a plot correlating the TD-DFT results for C_2H_4, obtained with different functionals, with the experimental values (from Ref. 62). The excitations considered are those starting from the $^1b_{3u}(\pi)$ orbital of ethylene. The most striking feature of this figure is the collapse of the BLYP and B3LYP excitation manifold above the corresponding $-\epsilon_{HOMO}$ values (6.61 and 7.67 eV for BLYP and B3LYP, respectively). In contrast, we do not find any abrupt collapse of the PBE0 excitation manifolds in our calculations; its energies are close to the MRCI values[62] and are also well above the energy of the HOMO (-7.9 eV, at the PBE0 level). The same general trend has been observed for H_2CO (see Fig. 2) and all the other molecules considered in the present study with fairly large basis sets, although we

have not explored the complete basis set limit. The potentials of conventional functionals can handle regions of space where the electron density is significant.[86,87] Evidently, the occupied KS orbitals are principally located in these regions, and so these orbitals and their energies are reasonably accurate. In contrast, the HOMO represents a more difficult task. As mentioned above, $-\epsilon_{HOMO}$ should correspond to the ionization potential in the limit of the exact potential. So the difference between these two quantities can be taken as a measure of the deviation of any model functional from the exact one. In Table XI we collected the ionization potentials (IP), computed as the energy differences between the neutral molecules and the corresponding cationic species, for the whole set of systems analyzed in this paper, together with the corresponding $-\epsilon_{HOMO}$ and experimental values. The results of Table XI show that, as expected, all DFT methods including PBE0 provide values of $-\epsilon_{HOMO}$ which are several eV below the IP. Nevertheless, the PBE0 model gives the values closest to experiments.

From another point of view, it must be pointed out that the introduction of some HF exchange leads to a significant improvement in the orbital eigenvalues over the corresponding pure functionals. The exact exchange-correlation potential is discontinuous as the number of electrons increases by

TABLE XI. Koopman ($-\epsilon_{HOMO}$) and vertical (vIP) ionization potential calculated with different functionals, using the Sadlej basis set. All vaues are in eV.

| | BLYP | | B3LYP | | PBE | | PBE0 | | |
Molecule	$-\epsilon_{HOMO}$	vIP	$-\epsilon_{HOMO}$	vIP	$-\epsilon_{HOMO}$	vIP	$-\epsilon_{HOMO}$	vIP	IP (exp)
CO	9.01	13.91	10.53	14.21	9.04	13.87	10.75	14.02	14.01
H_2CO	6.19	10.68	7.64	10.90	6.23	10.75	7.85	10.78	10.89
C_2H_4	6.61	10.56	7.67	10.60	6.77	10.69	7.90	10.52	10.51
$(CH_3)_2CO$	5.59	9.39	7.03	9.66	5.66	9.47	7.26	9.58	9.69
C_6H_6	6.14	9.10	7.08	9.27	6.33	9.28	7.30	9.26	9.24
C_5NH_5	5.79	9.21	7.20	9.55	5.89	9.31	7.45	9.50	9.34
$C_{10}H_8$	5.27	7.70	6.11	7.93	5.47	7.89	6.31	7.96	8.14

an integer.[88] The current pure functionals generate continuum potentials that are unable to exhibit such a discontinuity, and can only provide an average description.[89] As a consequence most of the current functionals do not have a correct long-range behavior, which strongly influences the energy of the virtual orbitals. The introduction of some HF exchange leads to a discontinuity in the potential, which partially corrects this behavior, thus significantly improving the results for orbital eigenvalues.

V. CONCLUSION

In the present work we have explored the behavior of the PBE0 functional on the evaluation of vertical excitation energies. The results obtained for a number of systems (both valence and Rydberg excitations) are in fairly good agreement with the experimental data and CASPT2 results. Furthermore, they are at least competitive with those delivered by other functionals, which include parameters specifically optimized for improving the long-range behavior of the exchange-correlation functional. We have thus shown that the PBE0 model is capable of describing photochemically interesting phenomena involving both valence and Rydberg excitations. From another point of view, these results, together with those already obtained for a wide class of chemical systems and properties[37–39,90] point out the advantages of using the same method (and almost the same basis set) to obtain different molecular features, ranging from geometries, to thermochemical data and vertical excitation energies.

ACKNOWLEDGMENTS

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