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Accurate Evaluation of Valence and Low-Lying Rydberg States with Standard Time-Dependent Density Functional Theory

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Using a standard exchange-correlation functional, namely, PBE0, the basis set dependence of time-dependent density functional theory (TD−DFT) calculations has been explored using 33 different bases and five organic molecules as test cases. The results obtained show that this functional can provide accurate (i.e., at convergence) results for both valence and low-lying Rydberg excitations if at least one diffuse function for the heavy atoms is included in the basis set. Furthermore, these results are in fairly good agreement with the experimental data and with those delivered by other functionals specifically designed to yield correct asymptotic/long-range behavior. More generally, the PBE0 calculations show that a greater accuracy can be obtained for both Rydberg and valence excitations if they occur at energies below the $\epsilon_{\mathrm{HOMO}} + 1$ eV threshold. This latter value is proposed as a thumb rule to verify the accuracy of TD−DFT/PBE0 applications.

1. Introduction

The accurate description of electronic excited states is of paramount importance in many fields of chemistry, including spectroscopy, photochemistry, or the design of new materials possessing optical properties. As a consequence, a large number of computational strategies have been developed to simulate excited-state properties, including electronic spectra of both organic and organometallic systems.[1] These methods range from the early semiempirical approaches, like CNDO/S or ZINDO, to the most recent and sophisticated post-Hartree−Fock (HF) methods, such as MRCI, EOM-CC, or CASPT2. As for other physicochemical properties, a reliable theoretical approach requires, to be routinely applicable, the combination of accurate results (or results affected by a constant error) with a reasonable amount of computer time/resources needed.

On the basis of the success encountered by density functional theory (DFT) for ground-state properties, time-dependent DFT (TD−DFT)[2] has gained a great popularity for excited state calculations, in particular among theoretical chemists. This approach, as the parent DFT one, combines a remarkable numerical precision in the evaluation of the excited-state properties, with a reasonable cost in terms of computational resources needed (i.e., time and hardware). As a matter of fact, large systems (up to 200 atoms or 2000 basis functions, in our experience), eventually including heavy transition metals, can be routinely studied on workstations. Such systems can hardly be analyzed at any other level of theory when requiring the same quality of results. Another, often underestimated, merit of TD−DFT is the lack of any kind preliminary assumption (or parametrization) on the nature of the excited electronic state. This last point is of particular relevance when the nature of the excited state is unknown and cannot be clearly deduced from experiments (see, for instance, ref 3).

However, several breakdowns have been attributed to the TD−DFT approach. These mainly concern the significant underestimations of the vertical excitation energies of Rydberg states and long-range charge-transfer (CT) transitions.[4−7] As for the failures of the parent DFT approach for ground-state properties, these problems mainly arise from the approximate nature of standard exchange-correlation functionals. In particular, these shortcomings have been traced back to an unsatisfactory description of the virtual Kohn−Sham (KS) orbitals and eigenvalues, arising from the asymptotically incorrect behavior of the most common potentials.[8] This latter requirement (asymptotic behavior) is also important for some DFT applications involving ground electronic state properties.[9] Additionally, the lack of inclusion of double excitations is another major problem typically related to the TD−DFT approach[10] that will not be addressed in the present paper.

Different methods and recipes have been developed to evaluate Rydberg and CT states within the TD−DFT framework from the use of asymptotically correct DFT potentials to the combination of DFT short-range components with long-range contributions.[8,11−20] Indeed, a partial cure is also represented by the use of the so-called hybrid functionals, where a fraction of Hartree−Fock (HF) exchange is plugged into the DFT functional.[21]

Different sources of error in the evaluation of transition energies, that is, approximations inherent to the TD−DFT approach, limits of the exchange-correlation functionals, and incompleteness of the basis set used, have been often erroneously mixed in the discussion about TD−DFT accuracy and have been attributed to a general breakdown of the TD−DFT approach itself.

In this paper, we want to show that a correct description of low-lying Rydberg states can actually be obtained even using common (hybrid) functionals provided that suitable basis sets are used. In particular, since the PBE0 functional[21,22] is, among the large number of hybrid approaches nowdays available, one of the most performing for excited-state calculations, this functional has been chosen for the present study. As a matter of fact, PBE0 provides, with astonishing accuracy, the UV−vis spectra for a wide range of organic compounds with the

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TABLE 1: List of the Used Basis Sets and of the Corresponding Number of Contracted Functions for the Considered Molecules[a]

basis set	highest angular momentum	molecules				
		CO	H_2CO	C_2H_4	C_5NH_5	C_6H_6
6-31G	1	18	22	26	64	66
6-31G(d)	2	30	32	38	100	96
6-31G(d,p)	2	30	38	50	115	114
6-31+G(d,p)	2	38	46	58	139	138
6-31+G(2d,p)	2	50	56	70	175	168
6-31+G(2d,2p)	2	50	62	82	190	186
6-31++G(2df,2pd)	3	64	88	124	267	264
6-31++G(3df,3pd)	3	76	104	148	318	312
6-311G	1	26	32	38	93	96
6-311G(d)	2	36	42	48	123	126
6-311G(d,p)	2	36	48	60	138	144
6-311+G(d,p)	2	44	56	68	162	168
6-311+G(2d,p)	2	54	66	78	192	198
6-311+G(2d,2p)	2	54	72	90	207	216
6-311++G(2df,2pd)	2	68	98	128	279	294
6-311++G(3df,3pd)	3	78	114	150	324	342
cc-pvdz	2	28	38	48	109	114
cc-pvtz	3	60	88	116	250	264
cc-pvqz	4	110	170	230	480	510
cc-pv6z	6	280	462	644	1295	1356
aug-cc-pvdz	2	46	64	82	183	192
aug-cc-pvtz	3	92	138	184	391	414
aug-cc-pvqz	4	160	252	344	710	756
aug-cc-pv6z	6	378	632	880	1769	1896
HD-SV(R)	2	36	40	44	64	120
HD-SVP(R)	2	46	56	66	118	168
HD-SVP(Rdif)	2	52	64	76	163	192
D-DZ(R)	2	54	42	46	186	126
D-DZP(R)	2	62	58	68	169	174
H-SV	1	18	22	26	64	66
H-SVP	2	28	38	48	109	114
H-TZV	1	28	34	40	99	102
H-TZVP	2	38	50	62	144	150

[a] For the acronyms, please refer to the text.

error being in some cases less than 0.1 eV.[23,24] Higher errors, albeit in an adequate range, have been found for organometallic complexes (error up to 0.3 eV).[25,26]

Therefore, in this contribution, fixing our choice of functional to PBE0, we will analyze the role played by the basis sets in the evaluation of Rydberg excitations. To this end, we have investigated the effect of basis set size and incompleteness in the energy evaluation of valence and low-lying Rydberg states, that is, states whose energy is close to the energy of the highest occupied molecular orbital, that is, ϵ(HOMO). Only standard, possibly not purposely tailored, and easily accessible basis sets were considered.

Five small, well-studied molecules, namely, carbon oxide, formaldehyde, ethylene, benzene, and pyridine, have been chosen as test cases. These molecules have been considered as prototypes for the analysis of valence $n-\pi^*$ and $\pi-\pi^*$ excitations as well as low-lying Rydberg transitions which are important for organic photochemistry.[12,14,15,18,23,27]

In our opinion, this contribution will help in fixing the lack of data concerning basis set effect on Rydberg excitation since, up to now, only a few papers have been devoted to a deep analysis of the basis set problem and mainly for valence excitations.[28−31]

2. Computational Details

All calculations have been carried out with the Gaussian program[32] using the PBE0 exchange-correlation functional.[21,22] This functional has been proven to give accurate vertical excitation energies for atoms, organic molecules, and organometallic complexes.[3,21,23,24,33,34] Molecular structures have been optimized using the 6-311+G(2d,2p) basis,[35] whereas different basis sets have been used for the calculations of excited states. These bases can be cast in four different classes: (1) Pople's split valence, both valence double-ζ (i.e., 6-31G) and triple-ζ quality (6-311G); (2) correlation consistent basis sets (cc), from double to sixth-ζ and corresponding augmented bases (aug-cc);[36] (3) Hay−Dunning (HD)/Dunning (D) bases,[37,38] including specifically optimized orbitals for Rydberg excitations (R); and (4) Ahlrichs single to triple z basis sets (H).[39,40] All the bases used are collected in Table 1 together with the corresponding numbers of contracted basis functions for each of the molecules analyzed and the highest angular momentum of the GTO basis.

Absorption spectra were computed as vertical excitations from the minima of the ground state using the TD−DFT approach as implemented in Gaussian using the basis set previously described.[41,42] These calculations have been carried out using an ultrafine grid for numerical integrals evaluation (corresponding to 99 radial shells and 590 angular points per shell), and at least 40 excited states were included in the Davidson diagonalization procedure of the TD−DFT excited-state matrix.

All the calculated vertical transitions have been evaluated by considering mean absolute errors (MAE) and root-mean-square (rms) deviations with respect to the experimental values. These latter have been taken from refs 12, 14, 15, and 21 to have more coherent comparisons with other theoretical data from literature.

3. Results

Before analyzing our results, it is worthwhile to add some comments on the choice of the exchange-correlation functional, here PBE0. Standard GGA and LDA functionals provide poor results when the excitations energies get close to the ionization threshold,[43] which, in the Koopman's approximation, corresponds to the opposite of the highest occupied molecular orbital (HOMO) energy. Using standard functionals, HOMO electrons are generally underbound because of a too rapid asymptotic decay of the exchange correlation potential, ν_{xc}, making the ionization threshold substantially too low.[44] These points have been well illustrated by Casida and Salahub several years ago.[8] The same authors pointed out the necessity of an exchange-correlation potential with the correct asymptotic behavior, that is, respecting the limit

$$\lim_{r \to \infty} \nu_{\mathrm{xc}}(r) = -\frac{1}{r}$$

Several approaches have been developed since then to design approximate but asymptotically corrected potentials and to improve the description of excited state in TD−DFT. The explored directions can be grouped in three large families. The first group collects all functionals whose potential (ν_{xc}) has the corrected asymptotic behavior, like that proposed by van Leeuwen and Baerends (LB),[17] on the basis of the analytical expression of Becke functional or that developed by Wu et al. and Yang and Wu from post-HF densities.[12,45] To the second family belong all the KS methods in which an explicit dependency of the orbitals is introduced in the exchange-correlation potential as the statistical averaging orbital potential (SAOP) approach.[46] This leads to KS models belonging to the fourth rung of the DFT improvement ladder, proposed by Perdew et al.[47]

Finally, the last family includes approaches forcing the potential to have the right behavior in an outer part and then seaming it with an unchanged inner part. The form of the connection and the nature of the description of the two parts to be connected determine the functional. So, for instance, the simplest model is represented by the HCTC(AC) functional, where the inner part is represented by a GGA functional and the outer part by HF exchange and the two are connected by a step function.[15] A more complex function is used in the gradient-regulated connection (GRAC) approach of Grüning et al., where the external LB functional is seamed with the Becke−Perdew GGA functional.[11] Finally, a very promising approach seems to be those of the long-range corrected (LC) functionals, initially developed by Adamson et al. and Leininger et al.[48,49] and more recently ameliorated by Yanai et al. and Tawada et al. (CAM family).[13,14] In such an approach, the exchange energy is split into short (E_{xS}) and long (E_{xL}) range contributions, computed in different ways. In fact, E_{xL} is evaluated from HF exchange integrals and the $\mathrm{erf}(\mu r_{12})/r_{12}$ operator, while the E_{xS} is a modified LDA or GGA functional.[13]

All these approaches have been tested for the calculation of absorption spectra. In particular, LC approaches are able to correct some of the failures of traditional DFT, especially concerning the calculation of Rydberg and charge-transfer excitations.[50,51,19]

Nevertheless, it is still difficult to get a clear and complete picture of functionals behavior in the description of valence, Rydberg, and charge-transfer excitations because of the lack of uniform tests and suitable benchmarks for excited states as currently available for other properties such as thermochemistry.

TABLE 2: Mean Absolute Error (MAE, eV) and Root Mean Square (rms, eV) Obtained When Computing the Lowest Seven Vertical Excitations of Carbon Oxide,[a] the Lowest Seven Vertical Excitations of Formaldehyde,[b] and the Lowest Nine Vertical Excitations of Ethylene[c]

	CO		H_2CO		C_2H_4	
basis set	MAE	rms	MAE	rms	MAE	rms
6-31G	3.25	4.47	2.30	2.86	3.11	3.76
6-31G(d)	3.20	4.44	2.28	2.82	3.02	3.66
6-31G(d,p)	3.20	4.44	2.25	2.80	3.69	4.37
6-31+G(d,p)	0.32	0.50	0.33	0.44	0.73	1.05
6-31+G(2d,p)	0.31	0.49	0.33	0.44	0.72	1.03
6-31+G(2d,2p)	0.31	0.49	0.33	0.43	0.71	1.00
6-31++G(2df,2pd)	0.32	0.48	0.29	0.42	0.50	0.67
6-31++G(3df,3pd)	0.33	0.46	0.30	0.41	0.47	0.61
6-311G	2.87	3.92	1.69	2.09	2.79	3.49
6-311G(d)	2.86	3.94	1.66	2.05	2.89	3.58
6-311G(d,p)	2.86	3.94	1.63	2.03	2.69	3.41
6-311+G(d,p)	0.33	0.51	0.32	0.42	0.62	0.77
6-311+G(2d,p)	0.32	0.50	0.31	0.42	0.61	0.76
6-311+G(2d,2p)	0.32	0.50	0.31	0.41	0.60	0.75
6-311++G(2df,2pd)	0.23	0.49	0.28	0.40	0.41	0.52
6-311++G(3df,3pd)	0.23	0.48	0.28	0.40	0.38	0.46
cc-pvdz	3.04	4.21	1.86	2.32	3.27	4.14
cc-pvtz	2.19	2.89	1.50	1.87	2.43	3.10
cc-pvqz	1.61	2.01	1.16	1.43	1.89	2.49
cc-pv6z	0.56	0.66	0.39	0.49	0.68	0.83
aug-cc-pvdz	0.34	0.43	0.32	0.43	0.42	0.54
aug-cc-pvtz	0.35	0.34	0.33	0.43	0.29	0.39
aug-cc-pvqz	0.26	0.33	0.38	0.44	0.22	0.26
aug-cc-pv6z	0.37	0.49	0.13	0.36	0.15	0.19
HD-SV(R)	0.54	0.64	0.48	0.55	0.44	0.52
HD-SVP(R)	0.51	0.64	0.50	0.59	0.52	0.59
HD-SVP(RDiff)	0.72	0.94	0.47	0.55	0.50	0.56
D-DZ(R)	0.41	0.59	0.49	0.55	0.44	0.52
D-DZP(R)	0.73	0.93	0.50	0.59	0.52	0.59
H-SV	2.91	3.94	1.93	2.38	3.38	4.27
H-SVP	2.87	3.94	1.87	2.32	3.12	4.06
H-TZV	1.52	1.98	1.36	1.61	2.24	2.79
H-TZVP	1.46	1.93	1.31	1.56	2.19	2.76

[a] Three valence and four Rydberg transitions, maximal transition energy = 12.40 eV. [b] Two valence and five Rydberg transitions, maximal transition energy = 9.22 eV. [c] One valence and eight Rydberg transitions, maximal transition energy=9.33 eV.

Another way to get a correction for the asymptotic potential is constituted by the use of hybrid functionals, where a fraction of HF exchange is included in the DFT scheme. In fact, as pointed out several years ago by Casida and Salahub,[8] hybrid functionals decay as $-a/r$, where a is a constant other than 1, representing the ratio between HF and DFT exchange. Even if this feature is common to all hybrids, the GGA functional fine-tunes the computed transitions so that the results obtained with different hybrids are not all of the same quality.[23] Among the available hybrid functionals, it has been shown that the PBE0 approach provides very accurate results for valence state transitions of a large number of organic and inorganic molecules. Furthermore, in an earlier study,[23] it was suggested, on the basis of a limited test set, that this functional could provide a correct evaluation of the low-lying Rydberg states. In this context, it would be interesting to more deeply investigate the possibility to have a unique approach to correctly describe both valence and Rydberg excitations for molecular systems. To this end, a clear vision of the effects of the other computational parameters, such as the basis sets, is mandatory.

3.1. Errors and Deviations on Computed Vertical Transitions: Overall Trends. The mean absolute (MAE) and the root-mean-square (rms) errors with respect to experimental values and as a function of the different basis sets used computed for the lowest vertical excitations of CO, H_2CO, and C_2H_4 are

TABLE 3: Mean Absolute Error (MAE, eV) and Root Mean Square (rms, eV) Obtained for the Lowest 19 Vertical Excitations of Pyridine[a] and the Lowest 15 Vertical Excitations of Benzene[b]

	pyridine				benzene			
basis set	valence	MAE Rydberg	all	RMS all	valence	MAE Rydberg	all	RMS all
6-31G	1.12	1.70	1.486	1.67	0.61	2.25	1.92	2.30
6-31G(d)	1.11	1.60	1.418	1.62	0.48	2.27	1.92	2.35
6-31G(d,p)	1.10	1.57	1.399	1.60	0.46	2.24	1.90	2.34
6-31+G(d,p)	0.19	0.25	0.226	0.31	0.25	0.31	0.30	0.39
6-31+G(2d,p)	0.18	0.22	0.20	0.30	0.24	0.26	0.26	0.36
6-31+G(2d,2p)	0.18	0.22	0.21	0.30	0.24	0.29	0.28	0.37
6-31++G(2df,2pd)	0.15	0.18	0.17	0.26	0.24	0.18	0.193	0.32
6-31++G(3df,3pd)	0.16	0.18	0.17	0.25	0.23	0.18	0.189	0.31
6-311G	0.74	1.16	1.01	1.14	0.52	1.55	1.342	1.63
6-311G(d)	0.70	1.10	0.95	1.11	0.37	1.45	1.234	1.55
6-311G(d,p)	0.68	1.08	0.93	1.10	0.35	1.46	1.238	1.56
6-311+G(d,p)	0.19	0.25	0.23	0.31	0.24	0.30	0.290	0.37
6-311+G(2d,p)	0.19	0.23	0.21	0.30	0.24	0.28	0.274	0.35
6-311+G(2d,2p)	0.18	0.22	0.21	0.30	0.23	0.28	0.271	0.34
6-311++G(2df,2pd)	0.15	0.16	0.16	0.25	0.23	0.17	0.179	0.29
6-311++G(3df,3pd)	0.15	0.16	0.16	0.25	0.24	0.16	0.171	0.28
cc-pvdz	0.83	1.33	1.15	1.35	0.57	1.54	1.350	1.51
cc-pvtz	0.65	0.98	0.86	1.03	0.49	1.14	1.011	1.15
cc-pvqz	0.51	0.74	0.65	0.79	0.45	0.86	0.782	0.93
cc-pv6z	0.43	0.60	0.54	0.66	0.44	0.75	0.69	0.86
aug-cc-pvdz	0.17	0.21	0.20	0.26	0.18	0.15	0.153	0.26
aug-cc-pvtz	0.20	0.18	0.19	0.24	0.19	0.14	0.148	0.22
aug-cc-pvqz	0.15	0.17	0.18	0.19	0.13	0.16	0.15	0.18
aug-cc-pv6z	0.11	0.13	0.12	0.15	0.09	0.11	0.11	0.14
HD-SV(R)	0.42	0.22	0.30	0.39	0.35	0.16	0.20	0.25
HD-SVP(R)	0.25	0.24	0.24	0.31	0.21	0.25	0.24	0.30
HD-SVP(RDiff)	0.26	0.24	0.25	0.31	0.21	0.25	0.24	0.30
D-DZ(R)	0.42	0.22	0.29	0.39	0.35	0.22	0.25	0.31
D-DZP(R)	0.26	0.24	0.25	0.31	0.21	0.24	0.23	0.30
H-SV	0.87	1.52	1.28	1.44	0.57	1.72	1.493	1.77
H-SVP	0.79	1.36	1.15	1.32	0.41	1.68	1.430	1.76
H-TZV	0.64	1.20	0.99	1.11	0.44	1.41	1.218	1.46
H-TZVP	0.62	1.10	0.93	1.08	0.28	1.29	1.088	1.35

[a] Seven valence and 12 Rydberg transitions, maximal transition energy = 8.03 eV. [b] Three valence and 12 Rydberg transitions, maximal exp transition rnergy = 7.81 eV.

reported in Table 2. MAE and rms of pyridine and benzene are collected in Table 3. Since the computed excitations include both valence and Rydberg transitions, the exact number of each type is specified in the table captions. In all cases, the energy of the highest computed vertical transition exceeds $-\epsilon_{\mathrm{HOMO}}$ at least 1.0 eV.

Let us first focus on the overall, that is, valence and Rydberg, rms and MAE computed using the different types of basis sets starting from the results obtained when the Pople ones: from the computed MAE and rms it is clear that standard double-ζ and triple-ζ bases (6-31G and 6-311G) yield very large errors (up to more than 4 eV for relatively simple systems such as C_2H_4). The inclusion of one or even more polarization functions, both on heavy and hydrogen atoms (that is d or d,p), only slightly affects the results (maximal variation of rms with respect to the 6-31G and 6-311G basis of about 0.05 eV), with the errors still being unacceptably large.

A dramatic improvement of the computed transitions is obtained only when adding one diffuse function on the heavier atoms (+). In this case, the errors drop to acceptable values, that is, always below 0.5 eV. On the other hand, no significant amelioration is noticed when adding additional polarization functions on hydrogen atoms (++). The only exception is constituted by C_2H_4 where the addition of a diffuse function also on hydrogen atoms is necessary to make the MAE drop below the 0.5 eV threshold. Furthermore, going from a double-ζ valence basis (6-31 type) to a triple-ζ quality one (6-311 type) still represents an improvement in absence of diffuse functions (i.e., when comparing the results obtained with the 6-31G, 6-31G(d), and 6-31G(d,p) with the corresponding 6-311G, 6-311G(d), and 6-311G(d,p) one). Adding at least one diffuse function actually smoothes the results obtained for double- and triple-ζ basis to similar errors. In other words, the MAE and rms computed when using the 6-31+G(d,p) or the 6-311+G(d,p) are very similar. Inclusion of additional polarization functions (from 2d,2p up to 3df,3pd) does not yield a substantial improvement.

To summarize, using split valence basis of Pople type, convergence of the MAE and rms with respect to the basis set is achieved when using at least a 6-31+G(d,p), the addition of a diffuse function being the crucial issue.

Moving to correlated consistent bases (cc-pv*X*z and aug-cc-pv*X*z, $X = 1-6$), the overall MAE and rms at convergence (i.e., when using at least a cc-pv6z or an aug-cc-pvqz) are similar to those obtained when using Pople type bases, even if the latter results in a smaller number of contracted basis functions.

Comparing the errors obtained with the cc- and corresponding aug-cc- bases, it is clear that, as previously discussed for the Pople bases, it is the inclusion of diffuse functions in the cc set (aug type) more than the addition of basis with higher angular momentum that drastically ameliorates the results. For instance, for CO while the simple addition of diffuse functions drops the rms (MAE) from 4.21 eV (3.04 eV) for the cc-pvdz to 0.43 eV (0.34 eV) for the aug-cc-pvdz one, it is necessary to go up to the cc-pv6z to obtain results of similar quality (rms = 0.66 eV, MAE = 0.56 eV). Similar trends are found for H_2CO, pyridine, and benzene (Tables 2 and 3).

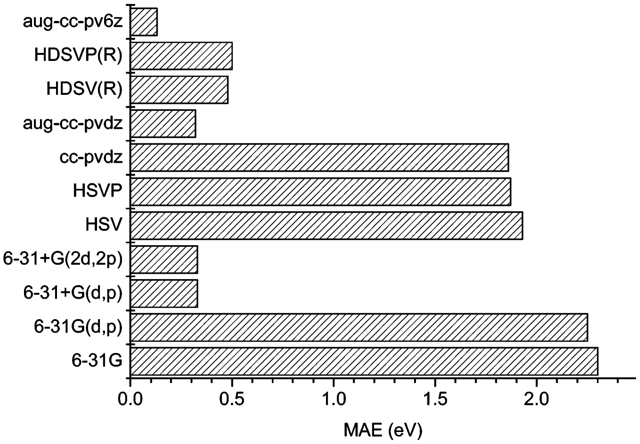

Figure 1. Mean absolute errors (MAE) for the computed vertical transitions in formaldehyde obtained with basis sets representative of the different families considered.

Generally, from the results obtained using both Pople and correlation-consistent bases, it seems that, to reduce the overall errors below a 0.5 eV threshold, it is necessary to include at least one diffuse p primitive function with an orbital exponent smaller than 0.05 on carbon and 0.07 on nitrogen atoms.

The excitation energies computed with the last two classes of basis sets (HD and H) further confirm these results. While none of the H bases lead to acceptable errors (MAE of 1.46 and 1.31 eV for CO and H_2CO, respectively, using the largest H-TZVP basis) because of the absence of diffuse p functions on heavy atoms, already the smallest HD basis (HD−SV(R)) yields MAE and rms of about 0.5 eV because of the presence of specifically tailored primitives for Rydberg excitations, that is, diffuse s, p, and d functions of carbon and nitrogen atoms (primitive s, p, and d exponents smaller that 0.03, 0.03, and 0.02 respectively). Indeed, the errors computed for HD and D basis are still larger than those computed using Pople basis of comparable size, as it can be noticed by comparing the MAE and rms computed for CO and H_2CO using the 6-31+G(d,p) and the HD−SV(R) basis or even the larger DZP(R) one.

Finally, a graphical overview of the performances obtained with basis sets representative of the four different families considered in this work is given in Figure 1, where the MAE on the computed vertical transitions is reported in the case of formaldehyde.

3.2. Vertical Transition Energies: Basis Set Effects on Valence and Rydberg Excitations. The errors discussed up to now stem both from valence and Rydberg excitations. To discuss separately the two contributions to the overall errors, partial MAEs, for both valence and Rydberg excitations, were computed in the case of pyridine and benzene, and they are collected in Table 3.

In the case of pyridine, Pople valence double-ζ valence bases (6-31G) offer a very poor description of both valence and Rydberg excitation unless diffuse functions are included at least on heavier atoms as shown in Figure 2 and in Table 3. This trend is confirmed in the case of benzene, although for this system the effect of diffuse functions on Rydberg transitions is significantly larger than on valence excitations, as it can be noticed by comparison of the MAEs computed with the 6-31G(d,p) and 6-31+G(d,p) bases (Table 3). The same holds when considering the triple-ζ valence series (6-311G type).

The correlation-consistent bases give, on average, smaller errors for valence excitations than those computed using Pople equivalent basis set. Indeed, the overall trends are still respected: larger errors are found for Rydberg excitation unless one includes diffuse functions on heavier atoms that more strongly affect Rydberg transitions than the valence ones.

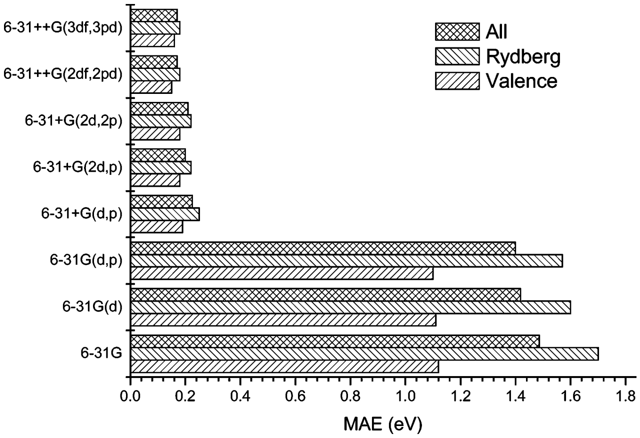

Figure 2. Evolution of the mean absolute errors (MAE) for the transition of pyridine computed with the 6-31G basis set family.

Indeed, one can still ask if the better performances obtained for valence excitations are because that, being normally lower in energy than Rydberg ones and far from the ionization potential of the molecule (IP = $-\epsilon_{\mathrm{HOMO}}$), they are simply not affected by the so-called asymptotic collapse or are intrinsic to their nature.

To this end, in Figure 3, we have reported the computed versus experimental transition for the full Pople double-ζ series of CO, H_2CO, C_2H_4, and pyridine together with the corresponding IP. The IPs, also reported in Table 4, were estimated as $-\epsilon_{\mathrm{HOMO}}$ computed with the largest basis of the Pople double-ζ family, that is, the 6-31++G(3df,3pd). Indeed, ϵ_{HOMO} value it is not very sensitive to the basis set, as evident when comparing the IP computed at 6-31G and 6-31++G(3df,3pd) in Table 4.

In the case of CO, Figure 3a, all transitions below the IP are correctly described even when using the smallest basis sets. On the other hand, for all the other systems, quite a large discrepancy with respect to experimental values is found for transitions with energies larger than ($-\epsilon_{\mathrm{HOMO}} - 1$ eV). In all cases, the agreement is drastically improved when adding a diffuse function.

To further analyze the data, in Figure 4, the computed transitions of benzene and pyridine are reported classed by their type (valence or Rydberg).

In the case of benzene, all valence excitations are below the IP, and the difference with respect to the experimental values is reasonably small even when using basis sets not including diffuse functions. In the case of pyridine, two valence transitions occur at energies higher than the IP of the molecule. These latter are very poorly described by bases up to 6-31G(d,p), and in this case the use of diffuse functions is compulsory also for the description of valence excitations, as previously noted from the results of Table 3.

Rydberg transitions, for both systems, are systematically wrongly described by the smaller bases with the use of diffuse functions being compulsory even when the transition energies are lower than the IP.

To summarize, valence excitations can be correctly recovered using basis sets without diffuse functions only if they lie below the $-\epsilon_{\mathrm{HOMO}}$ threshold; otherwise, diffuse functions should be added. On the other hand, a correct description of Rydberg transitions is obtained only when including diffuse functions, independently of their absolute energy, even if they are below the IP threshold.

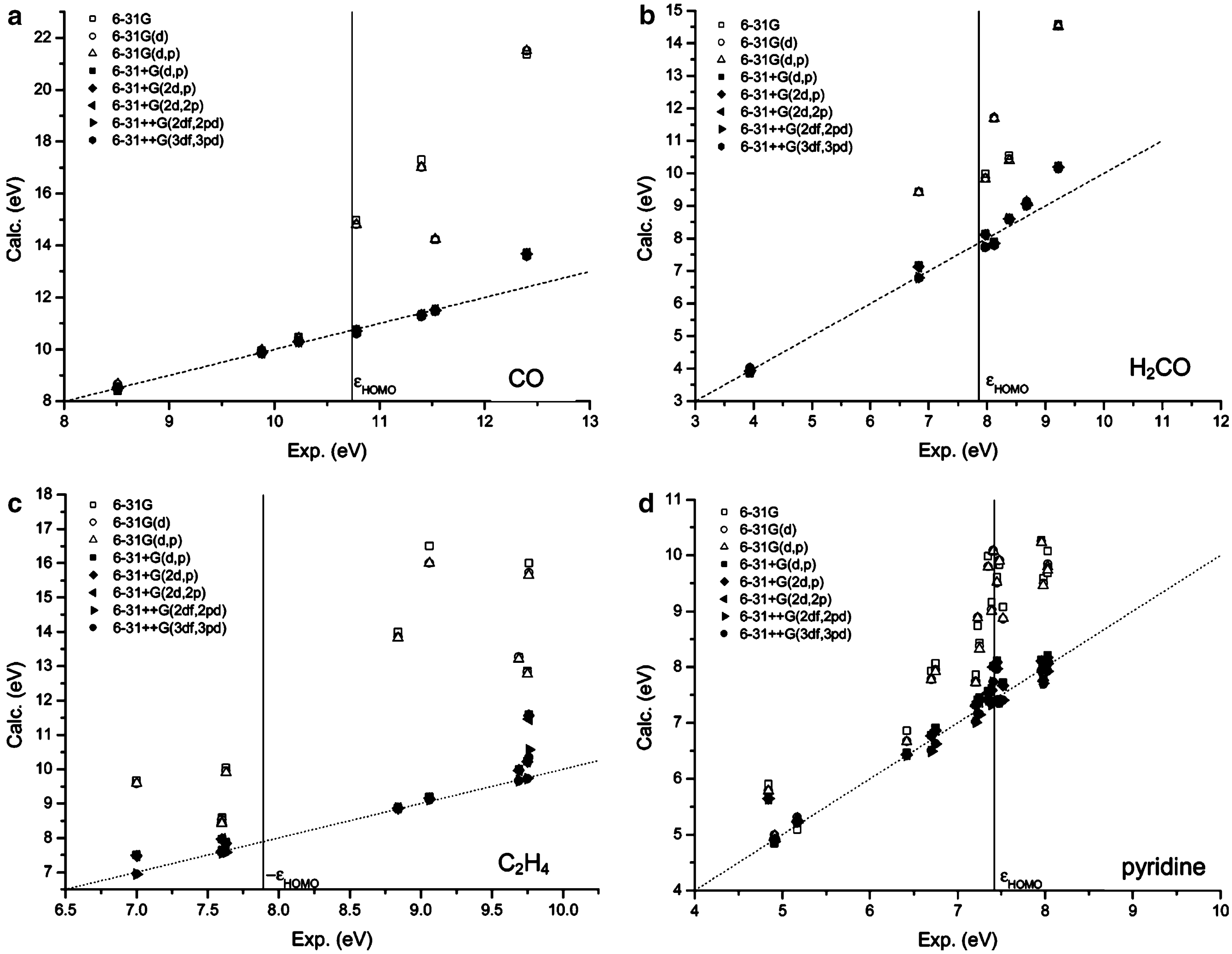

Figure 3. Computed versus experimental transitions for CO, H_2CO, C_2H_4, and C_5NH_5 using different Pople's basis sets.

TABLE 4: Energy of the Highest Occupied Molecular Orbital (HOMO, eV) of All the Considered Molecules

basis	CO	H_2CO	C_2H_4	C_5NH_5	C_6H_6
6-31G	−10.36	−7.62	−7.64	−6.97	−7.05
6-31++G(3df,3pd)	−10.74	−7.86	−7.89	−7.42	−7.27

Interestingly, the addition of only one diffuse function allows to significantly reduce the errors on all transitions up to ($-\epsilon_{HOMO} + 1$ eV). In Table 5, the MAEs computed using the 6-31++G-(3df,3pd) basis including all transitions up to ($-\epsilon_{HOMO} + 1$ eV) are all below the 0.3 eV threshold, thus showing that this computational protocol can successfully be applied for the description of both valence and low-lying Rydberg excited states.

3.3. Oscillator Strengths. Few papers in literature deal with the validation of a computational approach to get oscillator strengths at the TD−DFT level and only one,[52] at the best of our knowledge, discusses their dependency on the basis set. As a matter of fact, oscillator strengths are less frequently reported in literature than excitation energies are, since they are more difficult to obtain accurately at experimental level. Two notable exceptions are represented by the papers of Casida and Salahub[8] and Matsuzawa et al.[53] We refer the reader to the first article[8] for an accurate discussion of the problems related to the theoretical evaluation of oscillator strengths, while the experimental data, here considered and reported in Table 6, are taken from the second.[53]

In Table 6 are reported the oscillator strengths computed, at PBE0 level, using three different basis sets, all belonging to the Pople family, for selected transitions of H_2CO, C_2H_4, and benzene.

From the analysis of these data, the oscillator strengths are not particularly sensitive to the basis set used or, at least, not more than the vertical excitation energies are. In fact, oscillator strengths are already at convergence using the 6-31+G(d,p) basis with no noticeable change being present when going to the larger 6-311++G(3df,3pd) basis.

Once again, diffuse functions play a central role for the correct evaluation of oscillator strengths of Rydberg excitations more than for valence one that are computed at convergence already with the smaller 6-31G basis set. As it concerns the comparison with the experimental data, the agreement is good, especially when taking into account the experimental spreading of the data because of the intrinsic difficulties related to the experimental determination of oscillator strengths.

4. Comparison with TD−DFT Literature Data

As already mentioned, several functionals have been proposed either tailored for specific TD−DFT applications or designed to, more in generally, solve the drawbacks of standard TD−DFT approaches. Among the available data in literature, the values computed in this work using the standard PBE0/6-311++G(3df,3pd) approach are compared (Table 7) to those obtained by six specifically tailored approaches. They include

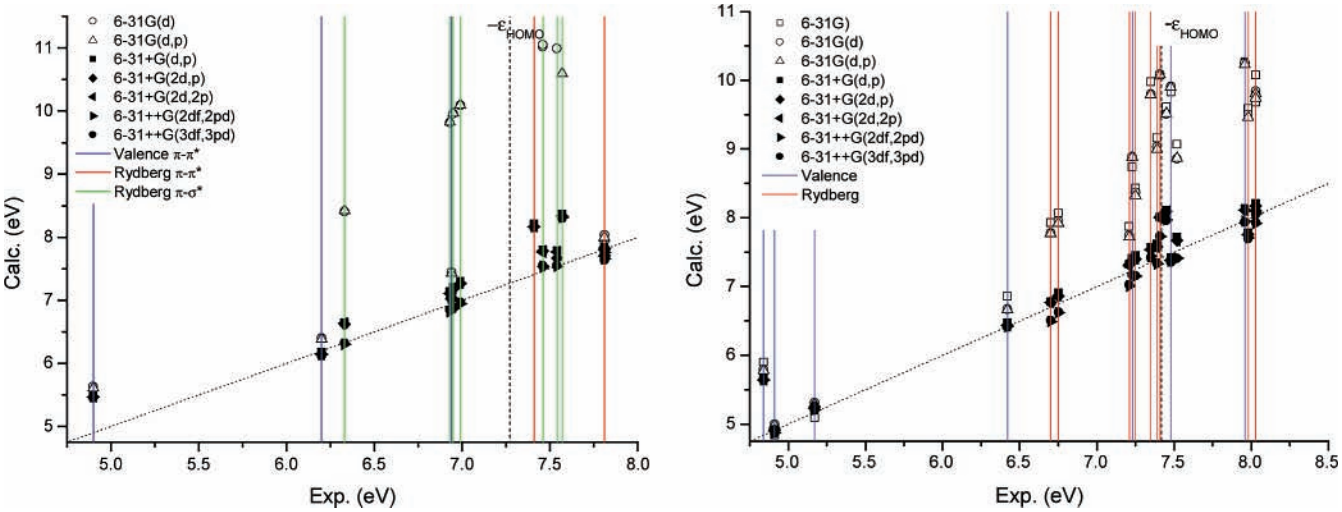

Figure 4. Computed versus experimental transitions for C_5NH_5 and C_6H_6 using different Pople's basis sets as function of the transition assignments (Rydberg or valence).

TABLE 5: Mean Absolute Error (MAE, eV) Computed for All the Molecules Considering All the Transitions with Energy Up to 1 eV above the HOMO Energy[a]

CO	H_2CO	C_2H_4	pyridine	benzene
0.06	0.30	0.26	0.17	0.19

[a] All data are computed with the 6-31++G(3df,3pd).

calculations carried out with the asymptotic-corrected functional of Tozer and Handy (HCTH(AC)),[15,54] a method based on the statistical average of orbital potential (SAOP),[46] the functional of Wu and Yang (WY) which uses the CCSD density as input for exchange-correlation potential evaluation,[12] and the gradient-regulated approach which connects the Becke−Perdew functional with that asymptotically corrected of van Leeuwen and Baerends (BPgracLB).[11] Finally, two long-range-corrected functionals have been also selected, the LC-BLYP and the LC-PBEOP,[14] with the latter including the one-parameter progressive correlation.[55] Of these six approaches, two, HCTH(AC) and BPgracLB, were specifically designed for the calculation of vertical transition energy calculations and, therefore, could not be very reliable for others properties, such as structure or thermochemistry.

In all cases, the basis set used includes diffuse functions and is close to the basis set limits and so makes the direct comparison of the MAEs meaningful.

As it clearly appears from the MAEs collected in Table 7, the PBE0 approach, coupled with the 6-311++G(3df,3pd), provides results which are of the same, if not better, quality than those obtained with more sophisticated protocols. Furthermore, the dispersion of the MAE is lower for PBE0. In particular, comparing the PBE0 approach with the LC family, the computed MAEs are particularly close, the H_2CO molecule possessing the highest MAE in both cases. Finally, even better results can be obtained with the very large aug-cc-pv6z. This latter basis, however, is too large for chemical applications (molecules with more than 15 atoms), thus suggesting that the Pople medium size basis represents the best compromise between accuracy and computed time.

5. Conclusion

In the present work, we have explored the dependence on basis sets of vertical excitation energies computed within the TD−DFT approach, using the standard PBE0 functional.

The results obtained for several systems show that to obtain reasonable valence and Rydberg excitations with energy up to $-\epsilon(\text{HOMO}) + 1$ eV, it is necessary to use PBE0 in conjunction with a basis set containing at least one diffuse function on heavier atoms. In fact, while valence excitations below the IP threshold can be correctly recovered using basis sets not including diffuse functions, a correct description of Rydberg transitions is obtained only when including diffuse functions, independently of the excitations' absolute energy, even if they are below the IP threshold. From a qualitative point of view, the need of inclusion of diffuse functions to describe Rydberg states is consistent with the classical picture where such a state corresponds to putting one electron into an orbit whose dimensions are very large, that is, diffuse, compared to the core. Indeed, the addition of diffuse functions can slightly increase the computational burden, especially in the case of very large organometallic systems.

The results obtained with such a computational protocol are in fairly good agreement with the experimental data and with those delivered by other functionals specifically designed to yield correct asymptotic/long-range behavior. These results, together other extensive studies carried out on valence excitations in organic molecules, suggest that the PBE0 could provide vertical transitions with an error bar that in the worst cases is around 0.1 eV for energies below the ionization threshold.

TABLE 6: Computed and Experimental Oscillator Strengths for Selected Vertical Transitions of H_2CO, C_6H_6, and C_2H_4[a]

molecule	transition	type	6-31G	6-31+G(d,p)	6-311++G(3df,3pd)	exp[b]
H_2CO	$1B_2$	R	0.1770	0.0288	0.0297	0.028,0.038, 0.0413, 0.032
	$1B_2$	R	0.0054	0.0286	0.0263	0.017, 0.017, 0.0281, 0.019
	$2A_1$	V	0.0490	0.0496	0.0484	0.032, 0.038, 0.0605, 0.036
C_6H_6	$1E_{1u}$	V	0.6015	0.6167	0.5960	1.20, 0.88, 0.86, 0.900
C_2H_4	$1B_{3u}$	R	0.0001	0.1320	0.0614	0.04
	$1B_{1u}$	V	0.3848	0.3524	0.3343	0.29

[a] R = Rydberg; V = valence type excitation. [b] Taken from ref 54.

TABLE 7: Mean Absolute Errors (MAE) for Vertical Excitations Obtained at Different Levels of Theory

method	CO	H_2CO	C_2H_4	C_5NH_5	C_6H_6
HCTH(AC)[a]	0.32	0.23	0.05		0.12
WY[b]	0.32	0.29	0.33		
SAOP[c]	0.09	0.14	0.25	0.25	0.53
BPgracLB[d]	0.09	0.23	0.16	0.34	0.21
LC-PBEOP[e]	0.54	0.44	0.17		0.28
LC-BLYP[e]	0.45	0.45	0.20		0.26
PBE0[f]	0.23	0.40	0.38	0.16	0.17

[a] From refs 15 and 55; augmented Sadlej basis set. [b] From ref 12; Sadlej + basis. [c] From ref 46 and ref 11. [d] From ref 11. [e] From ref 14; augmented Sadlej pVTZ basis. [f] This work; 6-311++G(3df,3pd) basis.

Furthermore, our calculations show that similar accuracy can be obtained for both Rydberg and valence excitations if they occur at energies below the $\epsilon_{\mathrm{HOMO}} + 1$ eV threshold. This latter value can be taken as a thumb rule to verify the accuracy of TD−DFT/PBE0 applications.

From another point of view, these results, together with those already obtained for a wide class of chemical systems and properties,[3,21,23,24,56−60] point out the advantages of using the same method (and often the same basis set) to obtain different molecular features ranging from geometries to thermochemical or spectroscopic properties.

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