Computationally Effective Functional and Basis sets for ORCA ESA Module Based Excited State Calculations

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Abstract

ESD module available in ORCA 5.0 is a potential choice for the siualtion of opto-electronic properties. As much it is effective and simple, it requires significant computational power to obtain results reasonable accuracy. In this work, we used a normal AMD Ryzen 7 machine to evaluate the accuracy and computational timings of the small benchmarking molecule benzene. Results indicate, B3LYP and PBE0 along with either 6-31G(d,p) or PC-1 could be vital choice for such highly restricted computational environment.

Introduction

The ESD module provided in ORCA 5.0.4 offers the possibility to calculate absorption, reorganization energy, HR factor, fluorescence, phosphorescence and inter-system crossing rates. However the module works well with the hybrid functional and better basis set. Such requirement limits the usage for bigger molecules and using low power computational settings

like a personal laptop. Here, we investigate the timing and performance (only for ground state) of different functional and basis sets using benzene as the model system.

Results and discussion

Methodology

All the calculations were carried out using a linux machine equipped with AMD Ryzen 7 processor with eight cores and sixteen threads. OpenMPI is used to parallelize the process. Though it offers threading to reach as maximum as 16 cores, only 4 real cores are used for all the calculations. Latest ORCA 5.0.4 version was used for all the calculations. B3LYP served as the initial functional and seven basis sets were used for the ground state geometry optimization. Of which four were selected for further analysis with nine more functional. From this six functionals and two basis sets were chosen for the excited state analysis. Since, we are not interested on the accuracy at this level, only the total run time is considered. A note of caution is that, these are very preliminary results and can vaguely guide the choice for functionals and basis sets rather than definitive guide for a potential choice.

Table 1: Performance of different basis sets with B3LYP functional. Difference (Diff) values are calculated by dividing the obtained value with experimental value.

Basis	Time	HOMO	LUMO	Eg	Diff
EXP		-9.2	1.1	-10.3	
6-31G	1m3s	-6.62	0.16	-6.78	0.658
SVP	1m3s	-6.87	-0.15	-6.72	0.652
PC1	1m33s	-7	-0.32	-6.68	0.648
PC2	5m24s	-6.99	-0.36	-6.63	0.643
TZVP	4m5s	-6.96	-0.3	-6.66	0.646
TZVPf	2m28s	-6.86	-0.37	-6.49	0.630
mTZVP	5m35s	-6.98	-0.37	-6.61	0.641

Table 2: Performance of different functionals with four different basis sets.

Functional	Basis	Time	HOMO	LUMO	Eg	Diff
PBE	6-31G	34s	-5.94	-0.75	-5.19	0.503
	SVP	36s	-6.2	-1.06	-5.14	0.499
	PC1	35s	-6.34	-1.2	-5.14	0.499
	TZVPf	1m5s	-6.27	-1.15	-5.12	0.497
PBE0	6-31G	1m6s	-7.02	0.22	-7.24	0.702
	SVP	1m4s	-7.26	-0.08	-7.18	0.697
	PC1	1m37s	-7.38	-0.23	-7.15	0.694
	TZVPf	2m27s	-7.27	-0.16	-7.11	0.690
REVPBE	6-31G	34s	-5.88	-0.71	-5.17	0.501
	SVP	35s	-6.14	-1.01	-5.13	0.498
	PC1	35s	-6.27	-1.15	-5.12	0.497
	TZVPf	1m5s	-6.19	-1.09	-5.1	0.495
M062X	6-31G	1m21s	-8.14	1.07	-9.21	0.894
	SVP	1m55s	-8.34	0.76	-9.1	0.883
	PC1	1m26s	-8.47	0.58	-9.05	0.878
	TZVPf	3m15s	-8.38	0.64	-9.02	0.875
CAMB3LYP	6-31G	1m23s	-8.19	1.44	-9.63	0.934
	SVP	2m4s	-8.43	1.11	-9.54	0.926
	PC1	1m25s	-8.55	0.93	-9.48	0.920
	TZVPf	2m57s	-8.5	0.93	-9.43	0.915
wB97X	6-31G	1m21s	-9.23	2.36	-11.59	1.125
	SVP	1m18s	-9.46	2.03	-11.49	1.115
	PC1	1m27s	-9.56	1.85	-11.41	1.107
	TZVPf	3m1s	-9.47	1.9	-11.37	1.103
TPSS0	6-31G	1m21s	-7.01	0.34	-7.35	0.713
	SVP	1m21s	-7.24	0.04	-7.28	0.706
	PC1	1m23s	-7.36	-0.1	-7.26	0.704
	TZVPf	3m10s	-7.25	-0.02	-7.23	0.701
PWP	6-31G	34s	-6.06	-0.87	-5.19	0.503
	SVP	36s	-6.32	-1.18	-5.14	0.499
	PC1	36s	-6.47	-1.34	-5.13	0.498
	TZVPf	1m5s	-6.42	-1.31	-5.11	0.496
wB97X-D3	6-31G	1m23s	-9.05	2.21	-11.26	1.093
	SVP	1m21s	-9.28	1.88	-11.16	1.083
	PC1	1m29s	-9.39	1.71	-11.1	1.077
	TZVPf	3m2s	-9.29	1.78	-11.07	1.074

Choice of basis sets

Our objective is find a functional and basis set that reasonably reproduces experimental HOMO, LUMO and their energy gap values and utilize the same to estimate the time taken by ESD module to simulate absorption spectrum for a single root. To start with, for geometry optimization, we have used B3LYP with seven basis, such as 6-31G(d,P), def2-SVP, PC-1, PC-2, def2-TZVP, def2-TZVP(-f) and def2-mTZVP (abbreviated as 6-31G, SVP, PC1, PC2, TZVP, TZVPf, mTZVP, respectively) for the analysis. The obtained results are given in Table. 1 along with the experimental data. It can be seen that four basis sets such as 6-31G, SVP, PC1 and TZVPf produced reasonable data with comparatively short span of time. So, these four are used with other functionals to test their efficiency.

Choice of functionals

Nine functional ranging from pure GGA to range separated and hybrid types such as PBE, PBE0, REVPBE, M062X, CAMB3LYP, wB97X, TPSS0, PWP, wB97X-D3 are used for the analysis. Obtained data is presented in Table. 2 (Difference (Diff) values are calculated by dividing the obtained value with experimental value.). Of which functionals such as PBE, REVPBE, TPSS0 and PWP optimizes the geometry in short span of time, their accuracy (in terms of Diff) is not reliable. So, only six functionals including B3LYP is selected for the excited state analysis.

Considering the four basis for different functionals, TZVPf consumes significant amount of time, especially with the heavy functionals like M062X and wB97X. It took the highest amount of time with the TPSS0 functional, yet the results are not on par with something like CAMB3LYP. Further, the D3 correction with wB97X consumes slightly more time and also improves the results bit better.

Of the chosen six functionals, basis 6-31G and PC1 performs on par with the time and accuracy. However, 6-31G performs slightly better in many cases than the PC1. The comparison between these two functionals is analyzed in the form of percentage difference analysis and

given in Fig. 1. For example in the case of B3LYP, PC1 is 32% more expensive than the 6-31G and 6-31 is 1.5 times more accurate than the PC1 results. CAMB3LYP is the only functional where both time and accuracy are almost equals for both the basis.
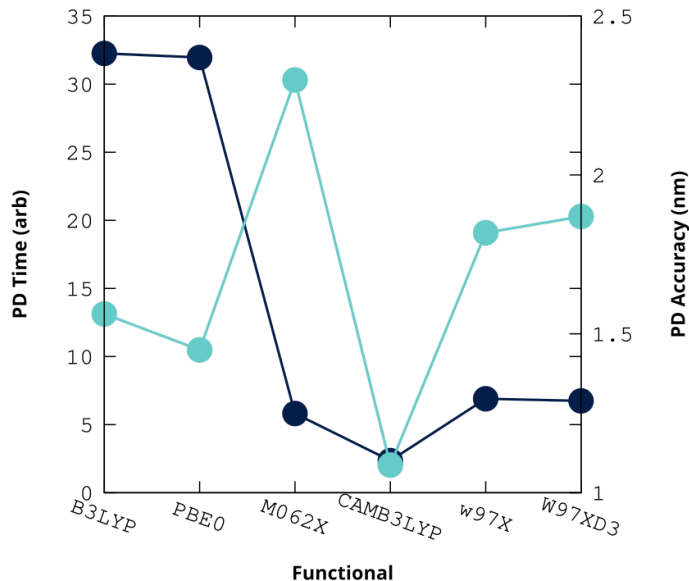

Figure 1: Percentage difference (PD) between 6-31G and PC1 for different basis sets. Dark blue represents time and light blue represents accuracy (i.e., energy gap).

Excited state calculations

Both 6-31G and PC1 were employed for the excited state calculations and obtained time required to complete the calculations is given in Table. 3.

Table 3: Time taken to complete the excited state calculations using different functionals and 6-31G and PC1 basis sets.

Functional	6-31G	PC-1
B3LYP	5m37s	5m42s
PBE0	6m7s	6m39s
M062X	NA	NA
CAMB3LYP	10m6s	9m34s
W97X	9m52s	10m50s
W97X-D3	9m58s	12m0s

Interestingly M062X is not supported by ESD (TD-DFT) module and calculations were failed in this case. On the other hand, both basis sets took almost similar time (yet PC1 is bit more expensive) to complete absorption spectrum calculations using ESD.

Experimental absorption maximum for benzene lies around 260. Though slightly blue shifted all the functionals faithfully produced spectra near to that value. Similarly, all the spectral data are slightly blue shifted with respect to B3LYP. The obtained spectrum are given in Fig. 2.
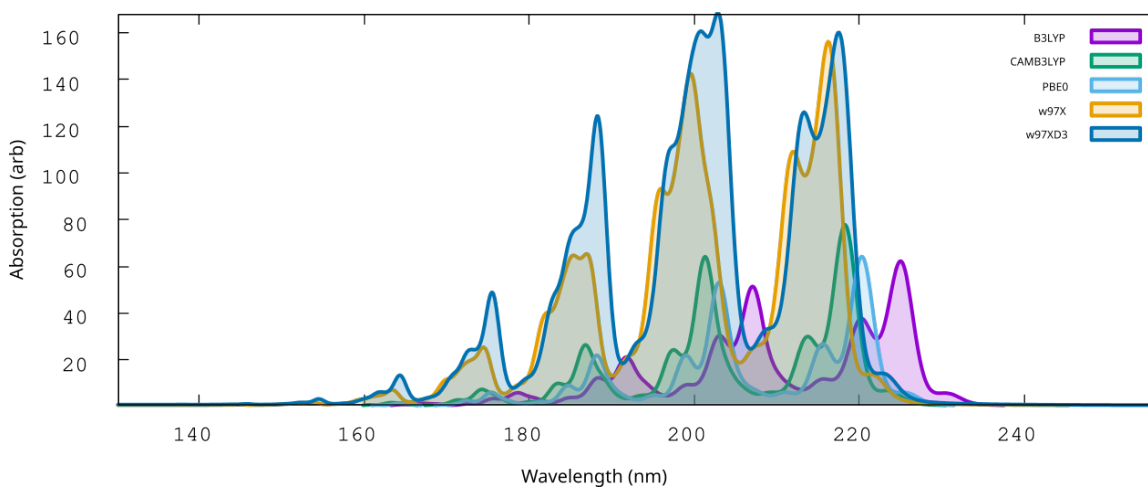

Figure 2: Absorption spectrum calculated using different functionals with 6-31G basis set.

Conclusions

ESD module is very useful in terms of simulating optoelectronic properties. On the other hand, unlike its predecessor ASA, it requires significant amount of computational power. In such case, the only way to acquire results by loosing accuracy. In this work, we investigated some standard functionals with minimal to medium level os basis sets. Even though we benchmarked the results with experimental data, actually we look for something better than routine B3LYP/6-31G(d,p) with similar or slightly higher computational requirement. While M062X seems promising but can not used for excited state calculations and w97X took almost twice the time of B3LYP for excited state calculations. Same is true in the

case of CAMB3LYP (which is much accurate than other methods considered in this work). So, we left out with two choices of either B3LYP or PBE0. PBE0 is slightly expensive and slightly better than B3LYP. So, it could be an alternate to B3LYP. On the other hand, in the case of basis sets both 6-31G and PC1 or in par with each other. However, similar to PBE0, if one can can afford slight expensive computational power, slightly better results can be obtained.

Supporting Information Available

Corresponding log files are deposited in Zenodo: