

Timings for SA-CASSCF, MC-PDFT, and CMS-PDFT Energy and Analytic Gradient Calculations in *OpenMolcas*

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The timings of several analytic gradient calculations are tested for phenol, C_6H_5OH . Two active spaces are tested, (12e, 11o) (60,984 configuration state functions (CSFs)) and (14e, 13o) (736,164 CSFs), and two basis sets are tested, jul-cc-pVDZ¹ (191 contracted basis functions) and jul-cc-pVTZ (406 basis functions). The basis sets are abbreviated as DZ and TZ in the rest of this document.

All calculations involve two states that are obtained from a state-averaged complete active-space self-consistent field (SA-CASSCF) calculation,² and this SA(2)-CASSCF calculation is used for both energy calculations and gradient calculations. Note that an MC-PDFT calculation for a state obtained from either a CASSCF or an SA-CASSCF calculation is formally called an MC-PDFT calculation, but only SA-CASSCF is employed for the calculations in this document. Also note that MS-PDFT is a short name for any multi-state PDFT calculation, including XMS-PDFT or CMS-PDFT.

For the timings presented here, the guess orbitals to start the SA-CASSCF iterations are the state-averaged natural orbitals from the converged SA-CASSCF calculation with the corresponding basis set and active space. For pair-density-functional calculations, numerical quadrature with 139,528 grid points is used to evaluate the on-top energies.

The timing for each calculation is recorded starting from the atomic-orbital integral calculation. For example, for a CMS-PDFT energy calculation, it includes an SA-CASSCF calculation as well as the time for the CMS-PDFT energy calculation; for a CMS-PDFT gradient calculation, it includes the time for SA-CASSCF and CMS-PDFT energy calculations as well as the time for a CMS-PDFT gradient calculation.

The calculations are performed with codes that are run serially with the MKL linear algebra library on the AMD cores of Minnesota Supercomputing Institute (MSI). The compiler used is gfortran and the following command is used for setting up the compiling environment.

```
cmake -D CMAKE_BUILD_TYPE=Release -D LINALG=MKL path/to/OpenMolcas/
```

The accelerated gradient code is referred to as the new code, and a previous, slow code is referred to as the old code. The identifiers for two codes are listed in Table 1.

Four methods, SA(2)-CASSCF, multiconfigurational pair-density functional theory (MC-PDFT),³ extended multistate pair-density functional theory (XMS-PDFT)⁴ and compressed-state multistate pair-density functional theory (CMS-PDFT),⁵ are tested for the energy calculations and SA-CASSCF,⁶ MC-PDFT⁷ and CMS-PDFT⁸ are tested for gradient calculations (the analytic gradient for XMS-PDFT calculation has not been implemented).

Table 1. Version identifiers for the old and the new versions of the *OpenMolcas* code used here. Version and tag are those that appear in output files, SHAR1 and commit number are found on <https://gitlab.com/Molcas/OpenMolcas/-/commits/master/src> and the commit number can also be found in the git log.

	Version	Tag	SHAR1	Commit
New	21.10	376-gb99d61a	b99d61a3	b99d61a3756cbccae920a67725fa413895d6fdd2
Old	21.10	250-g8502eb1	8502eb15	8502eb15c61dd86d4d9a8056a53afa4695eb0e41

Note that the CMS-PDFT gradient calculation is slower than the MC-PDFT gradient calculation because the gradient of each intermediate state is needed for a CMS-PDFT gradient calculation. This means that the time will grow linearly with respect to the number of states involved in the CMS-PDFT calculation. However, such linearity is not tested so no conclusion about the cost versus the number of states can be drawn from the data available.

Table 2. Timings (minutes) for the SA-CASSCF, MC-PDFT, MS-PDFT calculations for both energy and gradient calculations.^a

		SA(2)-CAS(12,11)/DZ		SA(2)-CAS(14,13)/DZ		SA(2)-CAS(12,11)/TZ		SA(2)-CAS(14,13)/TZ	
		New	Old	New	Old	New	Old	New	Old
Energy	SA-CASSCF	2		9		67		74	
	MC-PDFT	3	4	10	11	66	80	80	93
	XMS-PDFT	3	4	11	11	63	81	73	83
	CMS-PDFT	3	4	10	11	63	69	71	90
Gradient	SA-CASSCF	4		21		79		99	
	MC-PDFT	7	38	31	80	83	141	117	222
	CMS-PDFT	8	69	29	125	89	192	122	294

^a Note that some MC-PDFT or MS-PDFT energy calculations are slightly faster (<10%) than the SA-CASSCF calculation because less time is consumed for the SA-CASSCF iteration in the CMS-PDFT run. Such small variations can happen for various reasons, for example, the loading of the machine at the time the run was made.

Table 3. Ratio of the timing for a gradient calculation to that for an energy calculation for SA-CASSCF, MC-PDFT and CMS-PDFT. Ratios are computed from unrounded timings in seconds.

	SA(2)- CAS(12,11)/DZ		SA(2)- CAS(14,13)/DZ		SA(2)- CAS(12,11)/TZ		SA(2)- CAS(14,13)/TZ	
	New	Old	New	Old	New	Old	New	Old
SA-CASSCF	1.9		2.4		1.2		1.3	
MC-PDFT	2.1	9.6	3.2	7.3	1.3	1.8	1.5	2.4
CMS-PDFT	2.4	17.7	3.0	11.4	1.4	2.8	1.7	3.3

Table 4. Ratio of the timing for each gradient calculation to the timing for the SA-CASSCF gradient calculation. Ratios are computed from unrounded timings in seconds.

	SA(2)- CAS(12,11)/DZ		SA(2)- CAS(14,13)/DZ		SA(2)- CAS(12,11)/TZ		SA(2)- CAS(14,13)/TZ	
	New	Old	New	Old	New	Old	New	Old
SA-CASSCF	1.0		1.0		1.0		1.0	
MC-PDFT	1.6	9.2	1.5	3.7	1.0	1.8	1.2	2.2
CMS-PDFT	1.9	16.5	1.4	5.8	1.1	2.4	1.2	3.0

References

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