

Supporting Information: A robust, open-source implementation of the locally optimal block preconditioned conjugate gradient for large eigenvalue problems in quantum chemistry

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1 Calibration

In order to determine the number of vectors to add in the expansion space of the LOBPCG and Davidson-Liu algorithms, we performed numerical tests on the water molecule. In particular, we targeted a wide range of totalsymmetric electronic states at the Full CI level of theory with the frozen-core approximation, starting from 10 states and up to 100 by increments of 10. For each case, we performed various calculations trying to optimize a larger number of states than the targeted ones, hoping that this would aid the convergence path of themselves. The number of states in excess ranged from 0 to 50 by increments of 5. The basis set considered was Pople’s 6-31G*.

In figure 1, we report the total number of iterations required to converge Davidson (left panel) and LOBPCG (right panel), while in figure 2 we do the same for the total execution time in seconds. From the results, we note

2 LOBPCG

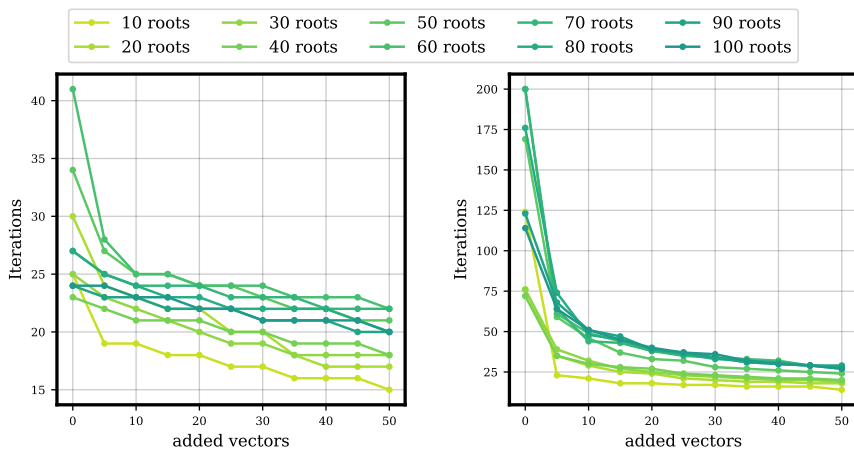


Fig. 1 Total number of iterations required to converge Davidson (left panel) and LOBPCG (right panel).

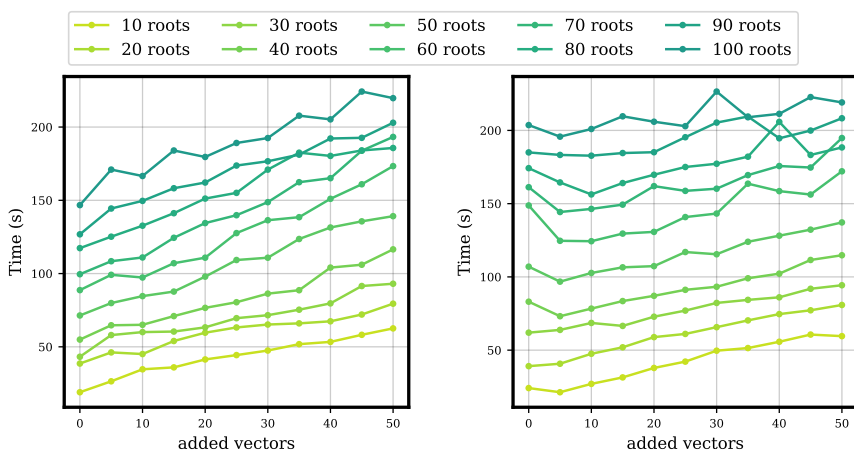


Fig. 2 Total time (in seconds) required to converge Davidson (left panel) and LOBPCG (right panel).

that LOBPCG is more sensitive to the number of added vectors. We find that adding five vectors is a reasonable compromise that allows LOBPCG to converge in a reduced number of iterations and an improved efficiency.

2 Geometries

We report below the geometries of the molecules used as numerical tests. Values are in Ångström.

FeC(CO)₃ (Z-matrix format)

FE

C 1 b1

C 1 b2 2 a1

C 1 b2 2 a1 3 d1

C 1 b2 2 a1 3 d2

O 1 b3 2 a2 3 d0

O 1 b3 2 a2 3 d1

O 1 b3 2 a2 3 d2

b1 = 1.559431159416771

b2 = 1.863860259772212

a1 = 102.791389437473597

d1 = 120.000000000000114

d2 = -120.000000000000114

b3 = 3.005607881132533

a2 = 101.188567425869721

d0 = 0.000000000000000

niacin

N 0.0770163088 -4.5354463974 -1.1070589214

C -0.4536326597 -3.4426343093 -1.7002377820

C 0.1345819156 -5.6676001196 -1.8419558236

C -0.9402074945 -3.4277362342 -3.0211325288

C -0.8772780607 -4.6053285233 -3.7772290593

C -0.3272022014 -5.7493672495 -3.1716972179

H 0.5657768045 -6.5440294213 -1.3520221902

H -1.3580230342 -2.5085637954 -3.4402327976

H -1.2386293840 -4.6575449078 -4.8074407533

C -0.2534375349 -7.0131246984 -3.9645966701

O 0.2946666968 -8.0424316245 -3.2555954593

O -0.6366232926 -7.1313597595 -5.1185349450

H -0.4899426835 -2.5368731876 -1.0864293628

H 0.2938546199 -8.8060097720 -3.8601064886

Nickel-based porphyrinoid

Ni 1.7345550 0.2053831 -0.1680936

F 6.4598840 -1.3871514 -2.2698142

F 6.3834863 -0.2270764 2.2826189

F 9.0036686 -0.7911953 2.4662908

F 10.3591021 -1.6568608 0.2893632

F 9.0796649 -1.9538618 -2.0777384

F -2.1157530 1.8290029 3.0562672

F -3.5156126 0.8275681 -1.3165970

N 3.2040829 1.2264695 -0.3333216

4 LOBPCG

N	0.8532261	1.7699155	-0.1117331
C	4.8896229	-0.4786071	-0.1112682
N	0.2869345	-0.7955393	0.1968809
F	-6.0416672	1.4473436	-0.6454036
F	-6.6130195	2.2636504	1.8716691
C	8.3761126	-0.9331622	1.3090200
N	2.6406507	-1.3398888	-0.0234606
C	0.4944385	-2.0752463	0.4792742
C	-0.5539479	3.4483738	0.2870792
H	-1.4500526	4.0100334	0.5003924
C	2.8775927	-3.4558782	0.6094077
H	2.6467877	-4.4611957	0.9217248
C	1.5809029	2.8778987	-0.1525130
F	-4.6424081	2.4530193	3.7176639
C	3.9850898	-1.5566177	0.0286479
C	1.9499951	-2.4118356	0.3427457
C	-0.4517568	2.0252281	0.1874030
C	4.3260363	3.1414321	-0.2568455
H	4.5475365	4.1956411	-0.2251655
C	6.3441606	-0.7876213	-0.0003819
C	-3.0603724	1.7358119	2.1304968
C	-1.6520890	-1.5851855	0.9550288
H	-2.6822731	-1.6534382	1.2681981
C	-0.9849589	-0.4071337	0.4943322
C	-1.3390443	0.9619864	0.4719807
C	-3.7701720	1.2198317	-0.0760352
C	3.0368988	2.5414260	-0.2890742
C	-0.7317037	-2.6208181	0.9485017
H	-0.9105196	-3.6379471	1.2566474
C	4.5197498	0.8756549	-0.2786706
C	-4.3601207	2.0569066	2.4861187
C	-5.0764567	1.5388748	0.2561809
C	4.1421224	-2.9257182	0.4110948
H	5.0769812	-3.4487917	0.5392251
C	-2.7385193	1.3123493	0.8482739
C	8.4145141	-1.5307950	-1.0140256
C	0.7094240	3.9775342	0.0803939
H	0.9781997	5.0208496	0.1065811
C	7.0635932	-1.2369127	-1.0990488
C	5.2474052	2.1068365	-0.2545932
H	6.3206268	2.2128040	-0.2246618
C	9.0708167	-1.3779764	0.1961931
C	7.0260411	-0.6427571	1.1998076
C	-5.3700746	1.9582856	1.5432705

Water (Z-matrix format)

O

H 1 b

H 1 b 2 a

b = 1.0

a = 104.5