

Supporting Information:
Accelerating geometry optimization via
Grassmann-DIIS extrapolation

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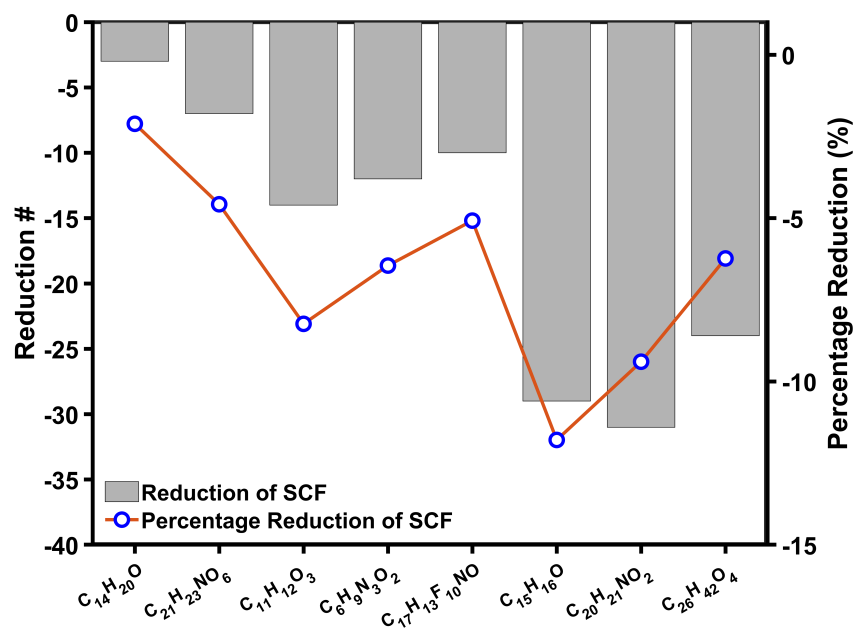
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Table S1: Total number of SCF iterations for Phenol(H₂O)₁₀ and (H₂O)₂₀ at B3LYP/def2-SVP levels using standard geometry optimization (OPT) and G-Ext-DIIS-augmented OPT with the core Hamiltonian matrix **H** and Coulomb matrix **CM**. Results are reported for different combinations of the length of the initial standard optimization phase (*i*) required for data accumulation and the number of historical density matrices (*k*) used in the extrapolation. The corresponding percentage reduction (PR) in SCF iterations, relative to the standard OPT procedure in which the MO coefficients from the preceding step are used as the initial guess for the current SCF calculation, is also reported.

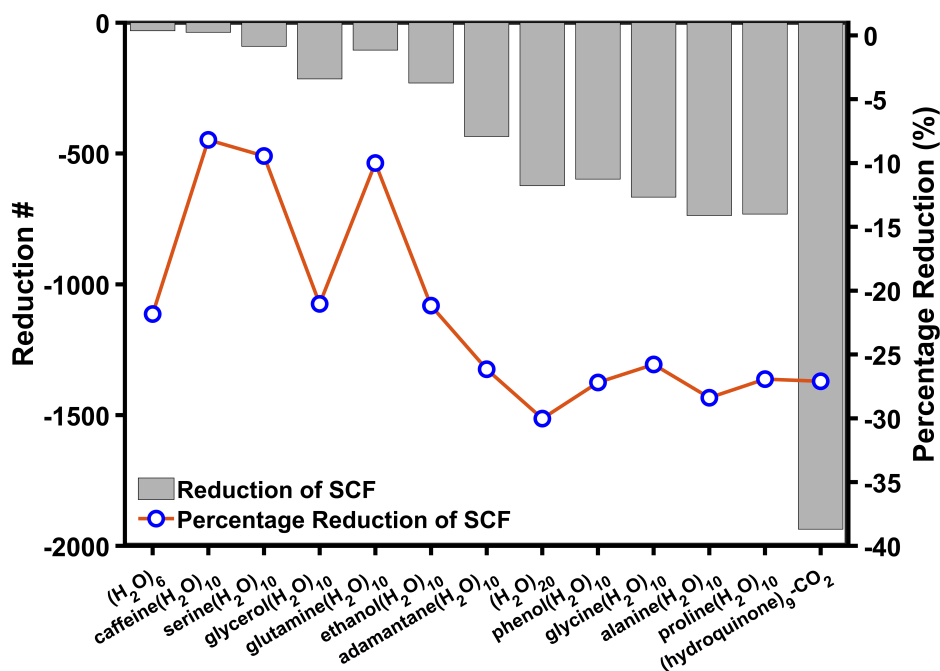
System	Standard OPT	<i>i</i>	<i>k</i>	G-Ext-DIIS			
				H	PR (%)	CM	PR (%)
Strategy-I							
Phenol(H ₂ O) ₁₀	2199	25	25	1752	-20.3%	2204	+0.23%
		20	20	1758	-20.1%	2206	+0.32%
		20	15	1764	-19.8%	2199	0.00%
		20	10	1834	-16.6%	2200	+0.05
		20	8	1847	-16.0%	2198	-0.05%
		20	5	1921	-12.6%	2201	+0.1%
		20	2	2064	-6.1%	2206	+0.32%
		10	10	1823	-17.1%	2199	0.00%
		10	8	1832	-16.7%	2204	+0.23%
		10	5	1913	-13.0%	2186	-0.59%
10	2	2051	-6.7%	2199	0.00%		
(H ₂ O) ₂₀	2075	25	25	1604	-22.7%	2060	-0.72%
		20	20	1605	-22.7%	2095	+0.96%
		20	15	1617	-22.1%	2062	-0.63%
		20	10	1657	-20.1%	2092	+0.82%
		20	8	1677	-19.2%	2092	+0.82%
		20	5	1765	-14.9%	2094	+0.92%
		20	2	1953	-5.9%	2061	-0.67%
		10	10	1669	-19.6%	2060	-0.72%
		10	8	1679	-19.1%	2059	-0.78%
		10	5	1765	-14.9%	2057	-0.87%
10	2	1951	-6.0%	2063	-0.58%		
Strategy-II							
Phenol(H ₂ O) ₁₀	2199	25	all	1634	-25.7%	2190	-0.41%
		20	all	1622	-26.2%	2194	-0.23%
		10	all	1615	-26.6%	2206	+0.32%
		8	all	1618	-26.4%	2205	+0.27%
		5	all	1610	-26.8%	2203	+0.18%
		2	all	1601	-27.2%	2204	+0.23%
(H ₂ O) ₂₀	2075	25	all	1478	-28.8%	2062	-0.63%
		20	all	1477	-28.8%	2098	+1.1%
		10	all	1466	-29.3%	2062	-0.63%
		8	all	1470	-29.2%	2055	-0.96%
		5	all	1456	-29.8%	2060	-0.72%
		2	all	1452	-30.0%	2053	-1.1%

Table S2: Total number of SCF iterations for Phenol(H₂O)₁₀ and (H₂O)₂₀ at PBE/def2-SVP and B3LYP/def2-TZVPPD levels using standard geometry optimization (OPT) and G-Ext-DIIS-augmented OPT with the overlap matrix descriptor **S**, core Hamiltonian matrix **H** and Coulomb matrix **CM**. Results are reported for different combinations of the length of the initial standard optimization phase ($i = 25, 20, 10, 8, 5,$ and 2) required for data accumulation and the number of historical density matrices ($k = \text{all}$) used in the extrapolation. The corresponding percentage reduction (PR) in SCF iterations, relative to the standard OPT procedure in which the MO coefficients from the preceding step are used as the initial guess for the current SCF calculation, is also reported.

System	Standard	i	k	G-Ext-DIIS					
				S	PR (%)	H	PR (%)	CM	PR (%)
PBE/def2-SVP									
Phenol(H ₂ O) ₁₀	3909	25	all	2975	-23.9%	3009	-23.0%	4025	+3.0%
		20	all	2963	-24.2%	3001	-23.2%	4099	+4.9%
		10	all	2962	-24.2%	2997	-23.3%	4055	+3.7%
		8	all	2958	-24.3%	2989	-23.5%	4070	+4.1%
		5	all	2955	-24.2%	2986	-23.6%	4050	+3.6%
		2	all	2938	-24.8%	2981	-23.7%	4094	+4.7%
(H ₂ O) ₂₀	2068	25	all	1524	-26.3%	1541	-25.5%	2100	+1.5%
		20	all	1511	-26.9%	1530	-26.0%	2103	+1.7%
		10	all	1501	-27.4%	1515	-26.7%	2107	+1.9%
		8	all	1499	-27.5%	1513	-26.8%	2110	+2.0%
		5	all	1492	-27.9%	1506	-27.2%	2111	+2.1%
		2	all	1487	-28.1%	1501	-27.4%	2111	+2.1%
B3LYP/def2-TZVPPD									
Phenol(H ₂ O) ₁₀	3018	25	all	2339	-22.5%	2325	-23.0%	3404	+12.8%
		20	all	2335	-22.6%	2323	-23.0%	3449	+14.3%
		10	all	2324	-23.0%	2297	-23.9%	3454	+14.4%
		8	all	2320	-23.1%	2292	-24.1%	3421	+13.4%
		5	all	2313	-23.4%	2291	-24.1%	3392	+12.4%
		2	all	2282	-24.2%	2271	-24.8%	3488	+15.6%
(H ₂ O) ₂₀	2695	25	all	2038	-24.2%	2162	-19.8%	3052	+13.2%
		20	all	2036	-24.5%	2153	-20.1%	2810	+4.3%
		10	all	2026	-24.8%	2054	-23.8%	3204	+18.9%
		8	all	1949	-27.7%	1939	-28.1%	3044	+13.0%
		5	all	1945	-27.8%	1936	-28.2%	3250	+20.6%
		2	all	1937	-28.1%	1932	-28.3%	3287	+22.0%



(a) Covalently Bonded Organic Molecules



(b) Noncovalently Bonded Clusters

Figure S2: Reduction and percentage reduction (%) in total SCF iterations between standard and G-Ext-DIIS-accelerated geometry optimization calculations using the core Hamiltonian matrix \mathbf{H} as the descriptor with the (2, all) setting at the B3LYP/def2-SVP level for (a) eight covalently bonded organic molecules and (b) 13 noncovalently bonded clusters. The systems are arranged from left to right according to the increasing total numbers of SCF iterations in the standard geometry optimization calculations, as reported in Table S3.

Table S3: Total number of SCF iterations for benchmark molecular systems at the B3LYP/def2-SVP level using standard geometry optimization (OPT) and G-Ext-DIIS-augmented OPT with the overlap matrix descriptor **S**, core Hamiltonian matrix **H** and Coulomb matrix **CM**. Results are reported for a combinations of the length of the initial standard optimization phase ($i = 2$) required for data accumulation and the number of historical density matrices ($k = \text{all}$) used in the extrapolation. The corresponding percentage reduction (PR) in SCF iterations relative to the standard OPT procedure using molecular orbital (MO) coefficients from the preceding optimization step as the initial guess is also reported.

System	Standard	<i>i</i>	<i>k</i>	G-Ext-DIIS					
	OPT			S	PR (%)	H	PR (%)	CM	PR (%)
Covalently Bonded Organic Molecules									
C ₁₄ H ₂₀ O	142	2	all	139	-2.11%	139	-2.11%	155	+9.15%
C ₂₁ H ₂₃ NO ₆	153	2	all	146	-4.58%	146	-4.58%	159	+3.92%
C ₁₁ H ₁₂ O ₃	170	2	all	156	-8.24%	156	-8.24%	173	+1.76%
C ₆ H ₉ N ₃ O ₂	186	2	all	175	-5.91%	174	-6.45%	190	+2.15%
C ₁₇ H ₁₃ F ₁₀ NO	197	2	all	188	-4.57%	187	-5.08%	208	+5.58%
C ₁₅ H ₁₆ O	246	2	all	217	-11.79%	217	-11.79%	256	+4.07%
C ₂₀ H ₂₁ NO ₂	330	2	all	298	-9.70%	299	-9.39%	372	+12.73%
C ₂₆ H ₄₂ O ₄	385	2	all	362	-5.97%	361	-6.23%	414	+7.53%
Noncovalently Bonded Clusters									
(H ₂ O) ₆	142	2	all	111	-21.83%	111	-21.83%	134	-5.63%
Caffeine(H ₂ O) ₁₀	452	2	all	412	-8.85%	415	-8.19%	472	+4.42%
Serine(H ₂ O) ₁₀	963	2	all	871	-9.55%	872	-9.45%	998	+3.63%
Glycerol(H ₂ O) ₁₀	1022	2	all	803	-21.43%	807	-21.04%	1070	+4.70%
Glutamine(H ₂ O) ₁₀	1050	2	all	946	-9.90%	945	-10.00%	1068	+1.71%
Ethanol(H ₂ O) ₁₀	1091	2	all	864	-20.81%	860	-21.17%	1197	+9.72%
Adamantane(H ₂ O) ₁₀	1663	2	all	1224	-26.40%	1228	-26.16%	1679	+0.96%
(H ₂ O) ₂₀	2075	2	all	1437	-24.50%	1452	-30.02%	2053	-1.06%
Phenol(H ₂ O) ₁₀	2199	2	all	1605	-27.01%	1601	-27.20%	2204	+0.23%
Glycine(H ₂ O) ₁₀	2587	2	all	1912	-26.10%	1920	-25.78%	2544	-1.66%
Alanine(H ₂ O) ₁₀	2596	2	all	1835	-29.31%	1859	-28.39%	2637	+1.58%
Proline(H ₂ O) ₁₀	2718	2	all	1987	-26.89%	1986	-26.93%	2707	-0.40%
(Hydroquinone) ₉ CO ₂	7144	2	all	5213	-27.03%	5208	-27.10%	7318	+2.44%

Table S4: Total number of SCF iterations for benchmark molecular systems at the B3LYP/def2-SVP level using standard geometry optimization (OPT) and G-Ext-DIIS-augmented OPT with the overlap matrix descriptor **S**, core Hamiltonian matrix **H** and Coulomb matrix **CM**. Results are reported for a combinations of the length of the initial standard optimization phase ($i = 2$) required for data accumulation and the number of historical density matrices ($k = \text{all}$) used in the extrapolation. The corresponding percentage reduction (PR) in SCF iterations, relative to the standard OPT procedure in which the superposition of atomic densities (SAD) method is used to generate the initial guess for each SCF calculation, is also reported.

System	Standard OPT			i	k	G-Ext-DIIS					
	SAD	MO	PR (%)			S	PR (%)	H	PR (%)	CM	PR (%)
Covalently Bonded Organic Molecules											
C ₁₄ H ₂₀ O	182	142	-21.98%	2	all	139	-23.63%	139	-23.63%	155	-14.84%
C ₂₁ H ₂₃ NO ₆	210	153	-27.14%	2	all	146	-30.48%	146	-30.48%	159	-24.29%
C ₁₁ H ₁₂ O ₃	210	170	-19.05%	2	all	156	-25.71%	156	-25.71%	173	-17.62%
C ₆ H ₉ N ₃ O ₂	225	186	-17.33%	2	all	175	-22.22%	174	-22.67%	190	-15.56%
C ₁₇ H ₁₃ F ₁₀ NO	252	197	-21.83%	2	all	188	-25.40%	187	-25.79%	208	-17.46%
C ₁₅ H ₁₆ O	308	246	-20.13%	2	all	217	-29.55%	217	-29.55%	256	-16.88%
C ₂₀ H ₂₁ NO ₂	459	330	-28.10%	2	all	298	-35.08%	299	-34.86%	372	-18.95%
C ₂₆ H ₄₂ O ₄	474	385	-18.78%	2	all	362	-23.63%	361	-23.84%	414	-12.66%
Noncovalently Bonded Clusters											
(H ₂ O) ₆	160	142	-11.25%	2	all	111	-30.63%	111	-30.63%	134	-16.25%
Caffeine(H ₂ O) ₁₀	630	452	-28.25%	2	all	412	-34.60%	415	-34.13%	472	-25.08%
Serine(H ₂ O) ₁₀	1274	963	-24.41%	2	all	871	-31.63%	872	-31.55%	998	-21.66%
Glycerol(H ₂ O) ₁₀	1417	1022	-27.88%	2	all	803	-43.33%	807	-43.05%	1070	-24.49%
Glutamine(H ₂ O) ₁₀	1358	1050	-22.68%	2	all	946	-30.34%	945	-30.41%	1068	-21.35%
Ethanol(H ₂ O) ₁₀	1677	1091	-34.94%	2	all	864	-48.48%	860	-48.72%	1197	-28.62%
Adamantane(H ₂ O) ₁₀	2366	1663	-29.71%	2	all	1224	-48.27%	1228	-48.10%	1679	-29.04%
(H ₂ O) ₂₀	2990	2075	-30.60%	2	all	1437	-51.94%	1452	-51.44%	2053	-31.34%
Phenol(H ₂ O) ₁₀	3150	2199	-30.19%	2	all	1605	-49.05%	1601	-49.17%	2204	-30.03%
Glycine(H ₂ O) ₁₀	3640	2587	-28.93%	2	all	1912	-47.47%	1920	-47.25%	2544	-30.11%
Alanine(H ₂ O) ₁₀	3850	2596	-32.57%	2	all	1835	-52.34%	1859	-51.71%	2637	-31.51%
Proline(H ₂ O) ₁₀	3990	2718	-31.88%	2	all	1987	-50.20%	1986	-50.23%	2707	-32.16%
(Hydroquinone) ₉ CO ₂	10598	7144	-32.59%	2	all	5213	-50.81%	5208	-50.86%	7318	-30.95%