Supporting Information: Low-Scaling Self-Consistent Minimization of a Density Matrix Based Random Phase Approximation Method in the Atomic Orbital Space

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1 Eigenvalue Spectra of the Approximated Hamiltonians and the RPA Hamiltonian

Table 1: Mean absolute deviations in Hartree of the eigenvalue spectra of the three approximated Hamiltonians from the ones of the RPA Hamiltonian for 44 molecules.

molecule	scRPA[$\tilde{\mathbf{H}}^{\mathrm{PBE}}$]	scRPA[$\tilde{\mathbf{H}}^{\mathrm{PBE0}}$]	scRPA[$\tilde{\mathbf{H}}^{\mathrm{HF}}$]
BH_2Cl	0.410626	0.314479	0.009522
BH_2F	0.44629	0.34254	0.00965
$BHCl_2$	0.450631	0.343705	0.014459
BHF_2	0.517411	0.395838	0.014028
CH_3Cl	0.428917	0.328835	0.008865
CH_3F	0.463563	0.355809	0.008685
CH_3OH	0.43177	0.332265	0.007307
ClCN	0.48826	0.372891	0.013544
ClF	0.578205	0.439101	0.023271
CO	0.495106	0.37877	0.012769
CS	0.442126	0.337223	0.014945
FCN	0.533763	0.407841	0.011937
H_2O-H_2O	0.45783	0.351073	0.009956
H_2O-NH_3	0.436086	0.335705	0.008134
H_2O	0.457004	0.351073	0.009801
H_2S-H_2S	0.415645	0.318268	0.010752
H_2S-HCl	0.436209	0.333374	0.012517
HCCF	0.483387	0.370564	0.009641
HCl−HCl	0.463429	0.353341	0.014874
HCl	0.461788	0.351914	0.015092
HCN	0.443651	0.340674	0.006957
HF−HF	0.539533	0.412479	0.014623
HF	0.537048	0.41037	0.014948
HOOH	0.497001	0.380374	0.01107
$LiBH_4$	0.315028	0.243353	0.003591
LiCl	0.325303	0.247803	0.013301
LiCN	0.350942	0.269983	0.00714

Table 1 Continued.

molecule	scRPA[$\tilde{\mathbf{H}}^{\mathrm{PBE}}$]	scRPA[$\tilde{\mathbf{H}}^{\mathrm{PBE0}}$]	scRPA[$\tilde{\mathbf{H}}^{\mathrm{HF}}$]
LiF	0.374755	0.287507	0.015355
LiH	0.215769	0.168318	0.002967
LiOH	0.341812	0.264857	0.011317
N_2H_4	0.434003	0.334158	0.007403
NaCl	0.335281	0.254466	0.017267
NaCN	0.357377	0.274389	0.010052
NaF	0.373639	0.292038	0.019897
NaH	0.225461	0.179105	0.00859
NaLi	0.165358	0.130699	0.006611
NaOH	0.346033	0.269366	0.014772
$NH_3{-}BH_3$	0.392471	0.302738	0.005272
$NH_3{-}NH_3$	0.4179	0.322133	0.006786
NH_3	0.417724	0.32184	0.006566
PH_3	0.390945	0.299887	0.008593
SF_2	0.583451	0.444077	0.023029
SiH_3Cl	0.412585	0.315366	0.011744
SiH_3F	0.443665	0.339619	0.011847
Mean	0.421245	0.323187	0.011351

2 Dipole Moments

Table 2: Dipole moments in Debye for 44 molecules calculated with the HF, PBE, PBE0, as well as the three different scRPA variants along the reference CCSD(T)/CBS values.[1] All calculations were performed with the cc-pV5Z basis set.

molecule	CCSD(T)	HF	PBE	PBE0	scRPA[$\tilde{\mathbf{H}}^{\mathrm{PBE}}$]	scRPA[$\tilde{\mathbf{H}}^{\mathrm{PBE0}}$]	scRPA[$\tilde{\mathbf{H}}^{\mathrm{HF}}$]
BH_2Cl	0.6838	0.9247	0.4342	0.5899	0.3391	0.3955	0.5317
BH_2F	0.8269	1.0129	0.6061	0.7445	0.6560	0.6985	0.7950
$BHCl_2$	0.6684	0.8699	0.4828	0.5976	0.4429	0.4649	0.5437
BHF_2	0.9578	1.1157	0.7705	0.8867	0.8045	0.8399	0.9195
CH_3Cl	1.8981	2.0524	1.8211	1.8911	1.6656	1.7004	1.7750
CH_3F	1.8083	1.9607	1.6432	1.7421	1.7456	1.7643	1.8155
CH_3OH	1.7091	1.8101	1.6004	1.6680	1.6761	1.6867	1.7203
ClCN	2.8496	3.1102	2.9592	2.9889	2.8171	2.8293	2.8976
ClF	0.8802	1.1347	0.7530	0.8507	1.0021	0.9678	0.9748
CO	0.1172	-0.2666	0.2209	0.0995	0.1928	0.2109	0.1775
CS	1.9692	1.6194	1.9971	1.9280	1.9877	2.0652	2.1233
FCN	2.1756	2.3383	2.3245	2.3054	2.1171	2.1005	2.1176
$H_2O{-}H_2O$	2.7303	2.8540	2.7624	2.7896	2.6638	2.6853	2.7322
$H_2O{-}NH_3$	3.5004	3.6342	3.5410	3.5757	3.4256	3.4519	3.5070
H_2O	1.8601	2.0025	1.8422	1.8945	1.8040	1.8261	1.8750
$H_2S{-}H_2S$	0.9181	0.9298	1.0690	1.0279	0.8768	0.8852	0.9004
$H_2S{-}HCl$	2.1328	2.1976	2.3368	2.3038	2.0358	2.0577	2.1008
HCCF	0.7452	0.8830	0.4541	0.6053	0.6408	0.6716	0.7425
HCl−HCl	1.7766	1.8705	1.8744	1.8770	1.6708	1.6911	1.7359
HCl	1.1055	1.2060	1.1133	1.1492	1.0326	1.0471	1.0830
HCN	3.0065	3.2911	2.9397	3.0364	2.9089	2.9161	2.9828
HF−HF	3.3991	3.5736	3.3836	3.4377	3.2814	3.3120	3.3808
HF	1.8059	1.9319	1.7685	1.8192	1.7296	1.7511	1.7989
HOOH	1.5732	1.6931	1.5511	1.5958	1.5065	1.5294	1.5762
$LiBH_4$	6.1281	6.2089	5.9477	6.0288	6.0713	6.1043	6.1561
LiCl	7.0960	7.2569	6.8193	6.9737	6.8220	6.8516	7.0107
LiCN	6.9851	7.1007	6.8077	6.9174	6.7647	6.8516	6.9600

Table 2 Continued.

molecule	CCSD(T)	HF	PBE	PBE0	scRPA[$\tilde{\mathbf{H}}^{\mathrm{PBE}}$]	scRPA[$\tilde{\mathbf{H}}^{\mathrm{PBE0}}$]	scRPA[$\tilde{\mathbf{H}}^{\mathrm{HF}}$]
LiF	6.2879	6.4490	6.0670	6.2011	6.0250	6.1048	6.2184
LiH	5.8286	5.9984	5.6100	5.7480	5.4698	5.6789	5.8495
LiOH	4.5664	4.6570	4.3182	4.4464	4.2973	4.3862	4.4897
N_2H_4	2.7179	2.8404	2.6585	2.7242	2.6273	2.6547	2.7138
NaCl	9.0066	9.2513	8.4834	8.7977	8.6244	8.7658	8.9326
NaCN	8.8903	9.0933	8.5817	8.7930	8.6043	8.7429	8.8898
NaF	8.1339	8.3700	7.7178	8.0147	7.5291	7.8596	8.0701
NaH	6.3966	7.0082	5.7572	6.2135	5.5441	5.9263	6.4434
NaLi	0.4837	0.6662	0.2059	0.3720	0.6701	0.3058	0.1906
NaOH	6.7690	6.8628	6.5010	6.6530	6.4933	6.6126	6.7199
$NH_3{-}BH_3$	5.2810	5.3729	5.2678	5.3029	5.1943	5.2160	5.2556
$NH_3{-}NH_3$	2.1345	2.2186	2.1642	2.1826	2.0670	2.0867	2.1256
NH_3	1.5289	1.6259	1.4932	1.5408	1.4590	1.4811	1.5242
PH_3	0.6069	0.6581	0.6369	0.6631	0.4723	0.4882	0.5214
SF_2	1.0555	1.3294	0.8414	0.9939	1.0988	1.0875	1.1403
SiH_3Cl	1.3645	1.4541	1.2187	1.3032	1.2116	1.2324	1.2869
SiH_3F	1.3123	1.4177	1.1785	1.2728	1.2344	1.2577	1.3133
MAD		0.1678	0.1616	0.0761	0.1650	0.1147	0.0504

References

(1) Hait, D.; Head-Gordon, M. How Accurate Is Density Functional Theory at Predicting Dipole Moments? An Assessment Using a New Database of 200 Benchmark Values. *J. Chem. Theory Comput.* **2018**, *14*, 1969–1981.