Electron Affinities with GPU-Accelerated Density-Fitting EOM-CCSD, Approximate EOM-CCSD Methods and EOM-CCSD with Frozen Natural Orbitals.

Support information

Yanmei Hu[1)], Zhifan Wang[2)] and Fan Wang[1,*)]

[1)]Institute of Atomic and Molecular Physics, Key Laboratory of High Energy Density Physics and Technology, Ministry of Education, Sichuan University, Chengdu 610065, People's Republic of China

[2)]College of Chemistry and Life Science, Chengdu Normal University, Chengdu 611130, People's Republic of China

[*)] **Corresponding author** : wangf44@gmail.com

Table SI: Electron affinities obtained from EOMEA-CCSD, corr-CIS(D_∞) and CIS(D_∞) calculations using aug-cc-pVXZ basis sets. (Unit: eV, aug-ccpVXZ(X = D, T and Q)

		aug-cc-pVDZ			aug-cc-pVTZ			aug-cc-pVQZ		
	th[a]	EOM-CCSD	corr-CIS(D_∞)	CIS(D_∞)	EOM-CCSD	corr-CIS(D_∞)	CIS(D_∞)	EOM-CCSD	corr-CIS(D_∞)	CIS(D_∞)
fumaronitrile	0.980	0.77	0.84	1.24	0.95	1.12	1.52	1.00	1.21	1.61
maleic anhydride	1.010	0.77	0.82	1.21	0.95	1.10	1.50	1.00	1.20	1.59
TCNE	3.050	2.91	3.04	3.61	3.12	3.34	3.90	3.18	3.44	4.00
benzoquinone	1.550	1.28	1.26	1.71	1.45	1.55	2.00	1.51	1.64	2.09
Cl_4-benzoquinone	2.480	2.23	2.32	2.92	2.39	2.59	3.19	2.46	2.69	3.29
F_4-benzoquinone	2.290	2.06	2.11	2.57	2.25	2.40	2.86	2.32	2.51	2.96
benzonitrile	-0.210	-0.41	-0.42	-0.34	-0.32	-0.31	-0.24	-0.26	-0.25	-0.19
F_4-benzenedicarbonitrile	1.620	1.46	1.54	1.99	1.66	1.83	2.28	1.73	1.93	2.38
mDCNB	0.610	0.43	0.46	0.91	0.60	0.74	1.19	0.65	0.83	1.28
nitrobenzene	0.540	0.30	0.22	0.69	0.47	0.50	0.99	0.53	0.61	1.08
nitrobenzonitrile	1.300	1.12	1.09	1.56	1.30	1.38	1.85	1.36	1.48	1.95
phthalic anhydride	0.870	0.63	0.63	1.09	0.80	0.91	1.38	0.85	1.01	1.47
C_{l4}-isobenzofurandione	1.680	1.47	1.55	2.15	1.63	1.82	2.42		1.92	2.52
phthalimide	0.630	0.38	0.36	0.84	0.54	0.64	1.13	0.60	0.74	1.22
dinitrobenzonitrile	1.760	1.60	1.67	2.16	1.78	1.95	2.45	1.84	2.05	2.54
naphthalenedione	1.470	1.19	1.17	1.68	1.35	1.45	1.95	1.41	1.55	2.05
azulene	0.540	0.39	0.36	0.83	0.53	0.61	1.08	0.57	0.70	1.17
dichlone	1.920	1.65	1.69	2.28	1.81	1.96	2.55	1.87	2.06	2.64
TCNQ	3.330	3.21	3.36	3.89	3.40	3.63	4.16	3.46	3.73	4.25
boron-dipyrromethene	1.670	1.46	1.40	1.84	1.61	1.67	2.11		1.75	2.19
NDCA	1.260	1.05	1.07	1.53	1.20	1.33	1.79		1.42	1.88
phenazine	1.110	0.86	0.76	1.27	1.02	1.04	1.56	1.07	1.14	1.65
acridine	0.690	0.45	0.40	0.88	0.60	0.67	1.15		0.76	1.24
anthracene	0.330	0.11	0.10	0.56	0.26	0.35	0.82	0.30	0.44	0.90

[a]Theoretical Value(CCSD(T)) of Ref. 19.

Table SII: Errors of FNO on EAs with EOMEA-CCSD and CIS(D_∞) using meanNOs and eaNOs with aug-cc-pVXZ basis sets. The error is defined as the difference between the EA of a method with FNO and that of the same method without FNO. (Unit: eV, aug-ccpVXZ(X = D, T and Q)

	meanNO						eaNO					
	aug-cc-pVDZ		aug-cc-pVTZ		aug-cc-pVQZ		aug-cc-pVDZ		aug-cc-pVTZ		aug-cc-pVQZ	
Mol	EOMEA-CCSD	CIS(D_∞)	EOMEA-CCSD	CIS(D_∞)	EOMEA-CCSD	CIS(D_∞)	EOMEA-CCSD	CIS(D_∞)	EOMEA-CCSD	CIS(D_∞)	EOMEA-CCSD	CIS(D_∞)
fumaronitrile	0.138	0.092	0.136	0.123	0.133	0.140	0.020	0.021	0.015	0.039	0.021	0.055
maleic anhydride	0.152	0.100	0.145	0.122	0.140	0.140	0.029	0.024	0.028	0.044	0.038	0.063
TCNE	0.146	0.092	0.125	0.123	0.135	0.146	0.008	0.021	0.009	0.040	0.022	0.057
benzoquinone	0.139	0.092	0.129	0.107	0.134	0.136	0.032	0.024	0.032	0.044	0.036	0.064
F_4-benzoquinone	0.126	0.083	0.119	0.117	0.135	0.152	0.021	0.019	0.026	0.040	0.033	0.058
Cl_4-benzoquinone	0.15	0.090	0.140	0.122	0.134	0.134	0.051	0.024	0.058	0.047	0.066	0.067
benzonitrile	0.077	0.074	0.041	0.042	0.044	0.046	0.006	0.016	0.008	0.021	0.009	0.023
F_4-benzenedicarbonitrile	0.136	0.088	0.127	0.122	0.124	0.131	0.040	0.022	0.044	0.043	0.050	0.060
mDCNB	0.132	0.090	0.119	0.114	0.118	0.132	0.021	0.020	0.017	0.037	0.023	0.053
nitrobenzene	0.152	0.099	0.130	0.111	0.132	0.141	0.026	0.021	0.026	0.041	0.030	0.061
nitrobenzonitrile	0.149	0.097	0.129	0.116	0.133	0.142	0.026	0.023	0.024	0.043	0.029	0.063
phthalic anhydride	0.138	0.090	0.129	0.113	0.127	0.136	0.028	0.022	0.028	0.042	0.031	0.060
Cl_4-isobenzofurandione	0.131	0.086	0.122	0.119		0.147	0.035	0.020	0.037	0.039		0.055
phthalimide	0.137	0.091	0.126	0.108	0.124	0.134	0.030	0.022	0.029	0.042	0.031	0.060
dinitrobenzonitrile	0.152	0.098	0.133	0.124	0.137	0.146	0.051	0.025	0.054	0.044	0.062	0.063
naphthalenedione	0.13	0.087	0.120	0.105	0.122	0.132	0.034	0.023	0.031	0.042	0.031	0.060
azulene	0.118	0.081	0.104	0.098	0.101	0.120	0.038	0.020	0.033	0.036	0.032	0.051
dichlone	0.126	0.083	0.114	0.104	0.122	0.135	0.029	0.020	0.030	0.040	0.032	0.057
TCNQ	0.121	0.079	0.108	0.106	0.116	0.129	0.022	0.022	0.019	0.040	0.027	0.057
boron-dipyrromethene	0.113	0.077	0.103	0.097		0.115	0.036	0.021	0.032	0.038		0.055
NDCA	0.131	0.089	0.117	0.108		0.130	0.023	0.023	0.019	0.041		0.058
phenazine	0.12	0.079	0.109	0.098	0.109	0.125	0.033	0.022	0.030	0.041	0.029	0.058
acridine	0.121	0.082	0.107	0.099		0.123	0.031	0.022	0.025	0.040		0.057
anthracene	0.125	0.087	0.106	0.100	0.103	0.121	0.030	0.022	0.022	0.040	0.022	0.055
ME	0.132	0.088	0.118	0.108	0.121	0.131	0.029	0.022	0.028	0.040	0.033	0.057
MAX	0.152	0.100	0.145	0.124	0.140	0.152	0.051	0.024	0.058	0.047	0.066	0.067
MIN	0.077	0.074	0.041	0.042	0.044	0.046	0.006	0.016	0.008	0.021	0.009	0.023

Explanation (pq|rs) and <pq|rs> of Equation 5:

Their precise definitions can be found on page 68 of the standard reference, Modern Quantum Chemistry: Introduction to Advanced Electronic Structure Theory.

$$（\mathrm{pq|rs}） = \int \varphi_{\mathrm{p}}(r_1)\varphi_q(r_1)\frac{1}{r_{12}}\varphi_r(r_2)\Psi\varphi_s(r_2)dr_1dr_2$$

$$\langle \mathrm{pq|rs} \rangle = \int \varphi_p(r_1)\varphi_q(r_1)\frac{1}{r_{12}}\varphi_r(r_2)\varphi_s(r_2)dr_1dr_2 = (\mathrm{pr|qs})$$

Here, p, q, r, and s are universal indices used to label molecular orbitals. The indices p and q represent the two orbitals associated with the first electron, while r and s represent the two orbitals associated with the second electron.