ELECTRONIC SUPPLEMENTARY INFORMATION

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How well can density functional theory and pair-density functional theory predict the correct atomic charges for dissociation and accurate dissociation energetics of ionic bonds?

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Table 1. Absolute energies *E* (in hartrees), Mulliken and dipole charges at 10 Å for NaCl

Methods	*E* (eq)/hartree	*E* (10 Å)/hartree	Mulliken charge	dipole charge
UHF	-621.4589	-621.3480	0.00	0.00
RHF	-621.4589	-621.3061	1.00	1.00
UMP2	-621.6849	-621.5364	0.00	0.00
CASSCF	-621.4673	-621.3420	0.00	0.00
CASPT2-0	-621.6934	-621.5382	0.00	0.00
CASPT2	-621.6923	-621.5343	0.00	0.00
UCCSD(T)	-621.7105	-621.5546	0.00	0.00
BLYP	-622.5939	-622.4891	0.46	0.45
PBE	-622.2878	-622.1784	0.47	0.46
revPBE	-622.4673	-622.3614	0.47	0.46
M06-L	-622.5873	-622.4560	0.63	0.61
revM06-L	-622.5676	-622.4365	0.51	0.50
MN12-L	-622.5162	-622.3954	0.53	0.52
MN15-L	-622.4846	-622.3652	0.52	0.52
HLE17	-632.5771	-632.4487	0.50	0.49
B3LYP	-622.6250	-622.5071	0.45	0.45
MN12-SX	-622.5291	-622.4075	0.55	0.54
HSE06	-622.3706	-622.2507	0.46	0.45
PBE0	-622.3401	-622.2165	0.45	0.44
M06[a]	-622.5612	-622.4313	0.54	0.54
MN15	-622.4138	-622.2784	0.49	0.48
BHandH	-620.9073	-620.7664	0.40	0.40
M08-HX	-622.5496	-622.4136	0.49	0.48
M06-2X	-622.5542	-622.4105	0.43	0.42
CAM-B3LYP	-622.6019	-622.4642	0.40	0.40
HISS	-622.4192	-622.2939	0.45	0.44
LC-ωPBE	-622.4029	-622.2518	0.00	0.00
LC-BLYP	-622.1615	-622.0079	0.00	0.00
ωB97X	-622.5850	-622.4302	1.00	0.99
M11	-622.5869	-622.4312	0.91	0.91
HFLYP	-622.5917	-622.4467	0.00	0.00
M06-HF	-622.5720	-622.4280	0.01	0.00
tPBE	-622.2739	-622.1232	0.00	0.00
trevPBE	-622.4553	-622.3075	0.00	0.00
tBLYP	-622.5755	-622.4312	0.00	0.00
ftPBE	-622.4090	-622.2546	0.00	0.00
ftrevPBE	-622.5902	-622.4392	0.00	0.00
ftBLYP	-622.7116	-622.5627	0.00	0.00

[a]Calculated with the aug-cc-pV(T+d)Z basis set

Table 2. (a) Absolute energies *E* (in hartrees) and dipole charges (*q*) for NaCl dissociation curve by UHF, PBE and UCCSD(T)

d/Å	UHF *E*	UHF *q*	PBE *E*	PBE *q*	UCCSD(T)[a] *E*
2.0	-621.4266	0.82	-622.2591	0.75	-621.6769
2.2	-621.4531	0.82	-622.2830	0.75	-621.7042
2.4	-621.4590	0.82	-622.2878	0.75	-621.7106
2.6	-621.4551	0.83	-622.2835	0.76	-621.7072
2.8	-621.4468	0.84	-622.2753	0.76	-621.6993
3.0	-621.4369	0.85	-622.2657	0.77	-621.6897
3.2	-621.4267	0.87	-622.2558	0.77	-621.6797
4.0	-621.3912	0.91	-622.2226	0.74	-621.6444
5.0	-621.3616	0.95	-622.1997	0.63	-621.6143
5.6	-621.3492	0.97	-622.1928	0.58	-621.6017
5.8	-621.3482	0.02	-622.1890	0.60	-621.5981
6.2	-621.3481	0.01	-622.1859	0.58	-621.5918
6.8	-621.3480	0.00	-622.1824	0.56	-621.5838
8.0	-621.3480	0.00	-622.1780	0.53	-621.5716
10.0	-621.3480	0.00	-622.1784	0.46	-621.5546

[a] UCCSD(T) charge is not computed.

(b) Absolute energies *E* (in hartrees) and dipole charges (*q*) for NaCl dissociation curve by CASSCF and tPBE

d/Å	CASSCF *E*	CASSCF *q*	tPBE *E*	tPBE *q*
2.0	-621.4353	0.82	-622.2447	0.82
2.2	-621.4615	0.82	-622.2690	0.82
2.4	-621.4674	0.82	-622.2739	0.82
2.6	-621.4637	0.83	-622.2695	0.83
2.8	-621.4557	0.83	-622.2611	0.83
3.0	-621.4460	0.84	-622.2511	0.84
3.2	-621.4359	0.86	-622.2408	0.86
4.0	-621.4005	0.90	-622.2047	0.90
5.0	-621.3693	0.95	-622.1722	0.95
6.2	-621.3483	0.98	-622.1502	0.98
6.4	-621.3454	0.98	-622.1472	0.98
6.6	-621.3428	0.98	-622.1445	0.98
6.8	-621.3421	0.01	-622.1243	0.01
8.0	-621.3420	0.00	-622.1234	0.00
10.0	-621.3420	0.00	-622.1232	0.00

Table 3. Absolute energies *E* (in hartrees) and Mulliken and dipole charges at 10 Å for AlO

Methods	*E* (eq) / hartree	*E* (10 Å) / hartree	Mulliken charge	dipole charge
UHF	-316.7866	-316.6981	0.00	0.00
ROHF	-316.7710	-316.6875	0.00	0.00
CASSCF	-316.9029	-316.7251	0.00	0.00
CASPT2	-317.1268	-316.9222	0.00	0.00
UHF-UCCSD(T)	-317.1169	-316.9290	0.00	0.00
W2X	-318.0676	-317.8718	0.00	0.00
BLYP	-317.6750	-317.4894	0.29	0.29
PBE	-317.4555	-317.2630	0.27	0.26
revPBE	-317.5924	-317.4096	0.26	0.25
B3LYP	-317.6839	-317.4985	0.18	0.18
PBE0	-317.4616	-317.2773	0.09	0.09
MN15	-317.4909	-317.2916	0.02	0.00
M06-2X	-317.6099	-317.4185	0.00	0.00
LC-ωPBE	-317.5148	-317.3265	0.00	0.00
LC-BLYP	-317.3070	-317.1090	0.00	0.00
HFLYP	-317.5911	-317.4487	0.00	0.00
M06-HF	-317.6310	-317.4438	0.00	0.00
tPBE	-317.4099	-317.2180	0.00	0.00
trevPBE	-317.5472	-317.3637	0.00	0.00
tBLYP	-317.6242	-317.4391	0.00	0.00
ftPBE	-317.4855	-317.2987	0.00	0.00
ftrevPBE	-317.6254	-317.4488	0.00	0.00
ftBLYP	-317.6975	-317.5153	0.00	0.00

Additional computational details

The KS-DFT calculations for all four molecules (NaCl, HF, LiH, and AlO) were performed using the UltraFine grid that has 99 radial shells and 590 angular points per shell.