

Supplementary Information for “Reaching the thermodynamic limit of periodic CCSD cohesive energies and band gaps”

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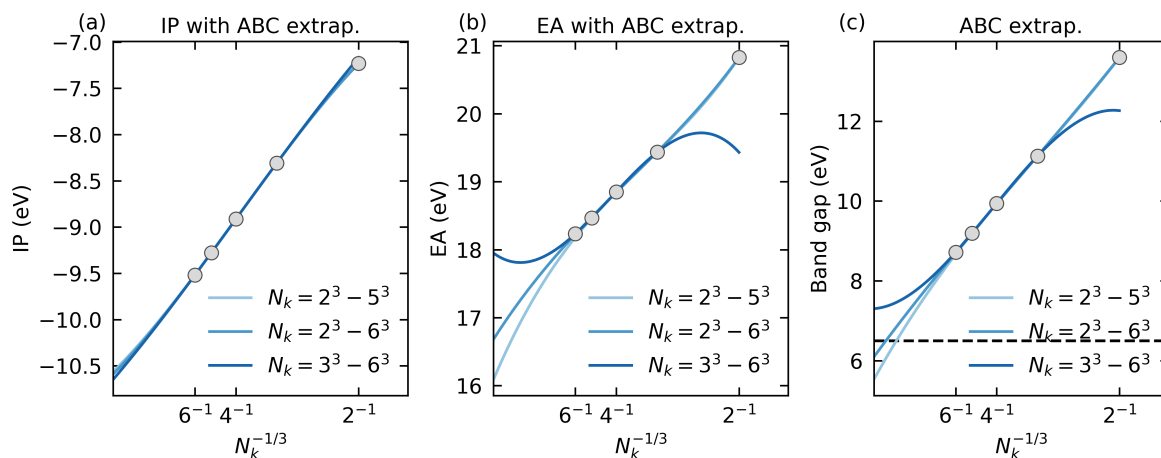


FIG. S1. Extrapolation curves of IP (at VBM), EA (at CBM), and indirect band gap (VBM to CBM) for BN obtained using the ABC extrapolation model with different k -mesh ranges. All calculations are carried out using the GTH-HF pseudopotential and the GTH-cc-pVDZ basis set. The black dashed line indicates the experimental band gap that is corrected for zero-point renormalization.

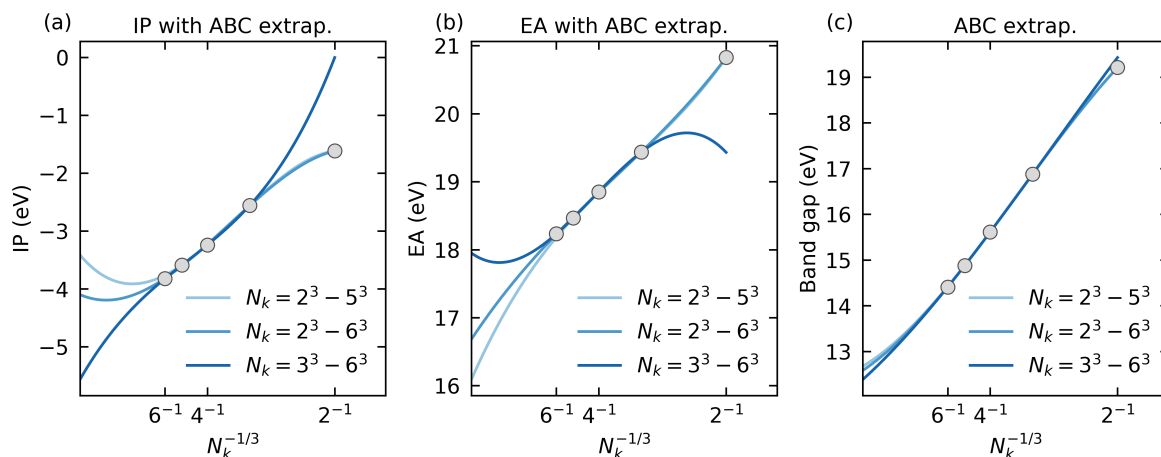


FIG. S2. Extrapolation curves of IP (at CBM), EA (at CBM), and direct band gap (at CBM) for BN obtained using the ABC extrapolation model with different k -mesh ranges. All calculations are carried out using the GTH-HF pseudopotential and the GTH-cc-pVDZ basis set.

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TABLE S1. Difference (TZ–DZ and QZ–DZ, in eV) between EOM-CCSD direct band gaps computed with the GTH-cc-pVDZ and GTH-cc-pVTZ basis sets for different systems and k -meshes. For BN, BP, Si, C, we compute the $\Gamma \rightarrow \Gamma$ direct band gap.

System	TZ–DZ				QZ–DZ		
	$N_k = 2^3$	$N_k = 3^3$	$N_k = 4^3$	$N_k = 5^3$	$N_k = 2^3$	$N_k = 3^3$	$N_k = 4^3$
MgO	−0.024	0.004	0.003	0.005	−0.003	0.032	0.034
LiCl	−0.069	−0.050	−0.048	−0.045	0.022	0.049	0.055
LiF	0.005	−0.007	−0.020	−0.026	0.064	0.055	0.045
LiH	−0.002	−0.002	0.002	0.004	−0.009	0.001	0.006
BN	0.024	0.042	0.052	0.057	0.062	0.083	N/A
BP	−0.061	−0.046	−0.036	−0.029	−0.060	−0.043	N/A
Si	−0.011	−0.013	−0.005	0.005	0.007	0.007	0.018
C	−0.063	−0.041	−0.032	−0.027	−0.067	−0.041	−0.030

TABLE S2. Conduction-band offsets (in eV) for different solids computed with different k -meshes. All calculations are carried out using the GTH-HF pseudopotential and the GTH-cc-pVDZ basis set.

k -mesh	BN	BP	Si	C (approx. k_{CBM})	C (k_{CBM})
$N_k = 2^3$	−5.293	−2.746	−2.510	−2.454	−2.487
$N_k = 3^3$	−5.351	−2.636	−2.463	−2.056	−2.141
$N_k = 4^3$	−5.303	−2.619	−2.441	−2.095	−2.164
$N_k = 5^3$	−5.321	−2.582	−2.405	−2.065	−2.114
$N_k = 6^3$	−5.320	N/A ^a	N/A ^a	−2.048	N/A ^a

^a Conduction-band energy at k_{CBM} is not available.

TABLE S3. Difference (TZ–DZ and QZ–DZ, in eV) between conduction-band offsets computed with the GTH-cc-pVDZ and GTH-cc-pVTZ basis sets for different systems and k -meshes.

System	TZ–DZ			QZ–DZ	
	$N_k = 2^3$	$N_k = 3^3$	$N_k = 4^3$	$N_k = 2^3$	$N_k = 3^3$
BN	−0.022	−0.001	−0.006	−0.025	−0.003
BP	−0.038	−0.059	−0.042	−0.031	−0.054
Si	0.006	0.010	0.025	0.018	0.021
C	0.010	−0.048	−0.010	0.018	−0.047

TABLE S4. Predicted cohesive energies (in eV/atom) obtained with the GTH-HF pseudopotential (PP) and the all-electron (AE) Hamiltonian at each level of theory, compared to previous literature results.

System	HF			MP2						CCSD		
	PP	AE	VASP [1]	PP	AE	VASP [1]	VASP [2]	FHI-aims [3]	PySCF [4]	PP	AE	VASP [2]
MgO	3.61	3.63	3.59	5.47	5.52	5.35			5.53	5.37	5.09	5.10
LiCl	2.70	2.71	2.70	3.70	3.72	3.64			3.70	3.69	3.52	3.55
LiF	3.32	3.34	3.34	4.56	4.61	4.49			4.54	4.58	4.38	4.50
LiH	1.79	1.79	1.79	2.38	2.39	2.39	2.39	2.38	2.41	2.45	2.50	2.45
BN	4.61	4.71	4.74	7.02	7.15	7.12	7.15	7.25	7.13	6.42	6.54	6.57
BP	3.37	3.40	3.38	5.59	5.64	5.61			5.77	5.58	4.89	4.95
Si	3.02	3.02	2.97	5.06	5.07	5.05			5.21	4.97	4.46	4.47
C	5.13	5.27	5.28	7.82	7.99	7.97	8.04	8.08	7.98	7.10	7.26	7.30

TABLE S5. Predicted EOM-CCSD band gaps (in eV) obtained with the GTH-HF pseudopotential (PP) and the all-electron (AE) Hamiltonian, compared to previous literature results. PySCF results from Ref. 5 used extrapolation model A with $N_k = 3^3-4^3$, and VASP and FHI-aims results from Ref. 6 used the GW-EOM-23 and GW-EOM-234 models, respectively.

System	PP	AE	PySCF [5]	VASP [6]	FHI-aims [6]
MgO	9.22	9.33	8.34	9.52	9.19
LiCl	10.18	10.36	9.43	9.90	
LiF	15.93	16.03	15.43	16.19	
LiH	6.28	6.21	5.85	6.26	6.32
BN	6.62	6.73	6.45	6.62	
BP	2.05	2.07	1.65	2.27	2.38
Si	1.29	1.23	0.96	1.29	
C	5.55	5.63	4.88	5.75	6.15

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