– Supporting Information for –

Real-space methods for ab initio modeling of surfaces and interfaces under external potential bias

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S1 Computational Details

As discussed in the main manuscript, the ONCV pseuodpotential used for the calculations performed in this work are from pseudo-dojo[1] and SPMS[2] repositories. The choice of pseudopotential used depends on the E_{cut} parameter obtained from a discretization study performed in `QE`. The pseudopotential data that required a lesser E_{cut} and thereby softer was used for all systems, as listed in Table S1.

Table S1: Pseudopotential used for benchmarking systems

S.No	Benchmarking system	Atom Types	Pseudopotential Repository
1	La-terminated LLZO	Li, La, Zr, O	SPMS[2]
2	(111) GaAs	Ga, As	SPMS[2]
3	(111) Al slab	Al	pseudodojo[1]
4	Na on (111) Al slab	Al, Na	pseudodojo[1]

S2 Benchmarking `CEF` setup

In this subsection, we benchmark the `CEF` method of applying an external potential bias against the sawtooth potential[3] used in `QE`, by comparing the differences in free energy, ionic forces, and dipole moments at various external electric fields. Our benchmarking shows excellent agreement in free energies, ionic forces, and dielectric response to the applied external field.

Slope ($\frac{\text{Ha}}{\text{bohr}}$)	Δ free energy ($\frac{\text{Ha}}{\text{atom}}$)	Δ ion force ($\frac{\text{Ha}}{\text{bohr}}$)	Δ dipole moment (D)
-0.0035	2.28×10^{-6}	3.36×10^{-5}	6.06×10^{-4}
-0.0025	2.28×10^{-6}	3.36×10^{-5}	9.79×10^{-4}
-0.00125	2.28×10^{-6}	3.36×10^{-5}	3.08×10^{-4}
0.00	2.28×10^{-6}	3.36×10^{-5}	-7.21×10^{-4}
0.00125	2.27×10^{-6}	3.36×10^{-5}	-6.89×10^{-4}
0.0025	2.27×10^{-6}	3.36×10^{-5}	-8.65×10^{-5}
0.0035	2.27×10^{-6}	3.36×10^{-5}	-6.97×10^{-4}

Table S2: Comparison of the differences in free energy, ionic forces and dipole moment between `QE` and `DFT-FE` for La-terminated LLZO slab.

Slope ($\frac{\text{Ha}}{\text{bohr}}$)	Δ free energy ($\frac{\text{Ha}}{\text{atom}}$)	Δ ion force ($\frac{\text{Ha}}{\text{bohr}}$)	Δ dipole moment (D)
-0.0035	2.28×10^{-6}	3.36×10^{-5}	6.06×10^{-4}
-0.0025	2.28×10^{-6}	3.36×10^{-5}	9.79×10^{-4}
-0.00125	2.28×10^{-6}	3.36×10^{-5}	3.08×10^{-4}
0.00	2.28×10^{-6}	3.36×10^{-5}	-7.21×10^{-4}
0.00125	2.27×10^{-6}	3.36×10^{-5}	-6.89×10^{-4}
0.0025	2.27×10^{-6}	3.36×10^{-5}	-8.65×10^{-5}
0.0035	2.27×10^{-6}	3.36×10^{-5}	-6.97×10^{-4}

Table S3: Comparion of the differences in free energy, ionic forces and dipole moment between QE and DFTFE for (111) GaAs slab.

Slope ($\frac{\text{Ha}}{\text{bohr}}$)	Δ free energy ($\frac{\text{Ha}}{\text{atom}}$)	Δ ion force ($\frac{\text{Ha}}{\text{bohr}}$)	Δ dipole moment (D)
-0.008	2.89×10^{-5}	3.36×10^{-5}	1.45×10^{-3}
-0.004	2.89×10^{-5}	3.36×10^{-5}	2.55×10^{-4}
-0.002	2.89×10^{-5}	3.36×10^{-5}	-3.81×10^{-4}
-0.001	2.89×10^{-5}	3.36×10^{-5}	1.54×10^{-4}
0.00	2.89×10^{-5}	3.36×10^{-5}	2.11×10^{-4}
0.001	2.89×10^{-5}	3.36×10^{-5}	1.28×10^{-4}
0.002	2.89×10^{-5}	3.36×10^{-5}	-1.07×10^{-3}
0.004	2.89×10^{-5}	3.36×10^{-5}	8.38×10^{-5}
0.008	2.89×10^{-5}	3.36×10^{-5}	1.66×10^{-3}

Table S4: Comparion of the differences in free energy, ionic forces and dipole moment between QE and DFTFE for (111) Al FCC slab.

References

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(3) Kunc, K.; Resta, R. External fields in the self-consistent theory of electronic states: a new method for direct evaluation of macroscopic and microscopic dielectric response. *Physical Review Letters* **1983**, *51*, 686.