Supporting Information

First-Principles Insights into Dopant-Vacancy Interactions in Acceptor-Doped Perovskites

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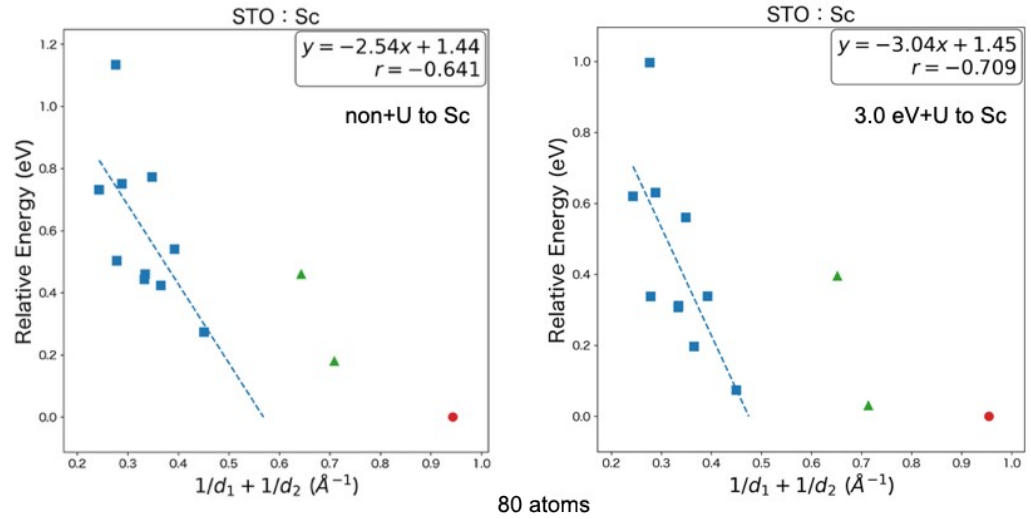
Table S1: Host structures and the dopant cations.

Host material	Dopant (A-site doping)		Dopant (B-site doping)	
	Group 1	Group 2	Group 1	Group 2
$LaAlO_3$	Sr^{2+}	Ba^{2+}	Mg^{2+}	Cu^{2+}
$LaGaO_3$	Sr^{2+}	Ba^{2+}	Mg^{2+}	Cu^{2+}
$SrTiO_3$	Na^{+}	K^{+}	Sc^{3+}	Fe^{3+}

Table S2: Initial phase, supercell scaling factor, and k-point grid used for structural relaxation of each host material

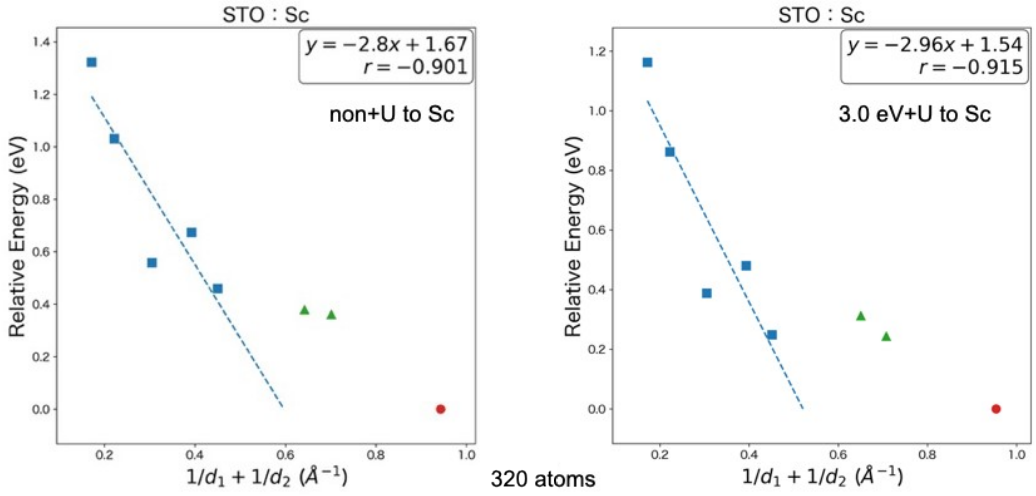
Host material	Phase	repetition	k-point grid
$LaAlO_3$ (800 K)	Pm3_m	2*2*4	4*4*2
$LaAlO_3$ (0 K)	R3_c	※	3*3*4
$LaGaO_3$ (800 K)	R3_c	※	4*4*2
$LaGaO_3$ (0 K)	Pnma	2*2*1	3*3*4
$SrTiO_3$ (800 K)	Pm3_m	2*2*4	4*4*2
$SrTiO_3$ (0 K)	I4/mcm	2*2*1	3*3*4

Figure S1: Comparison of trends for STO with 80 and 320 atoms in the supercell and Sc without DFT+U correction and 3.0 eV Hubbart correction.



80 atoms

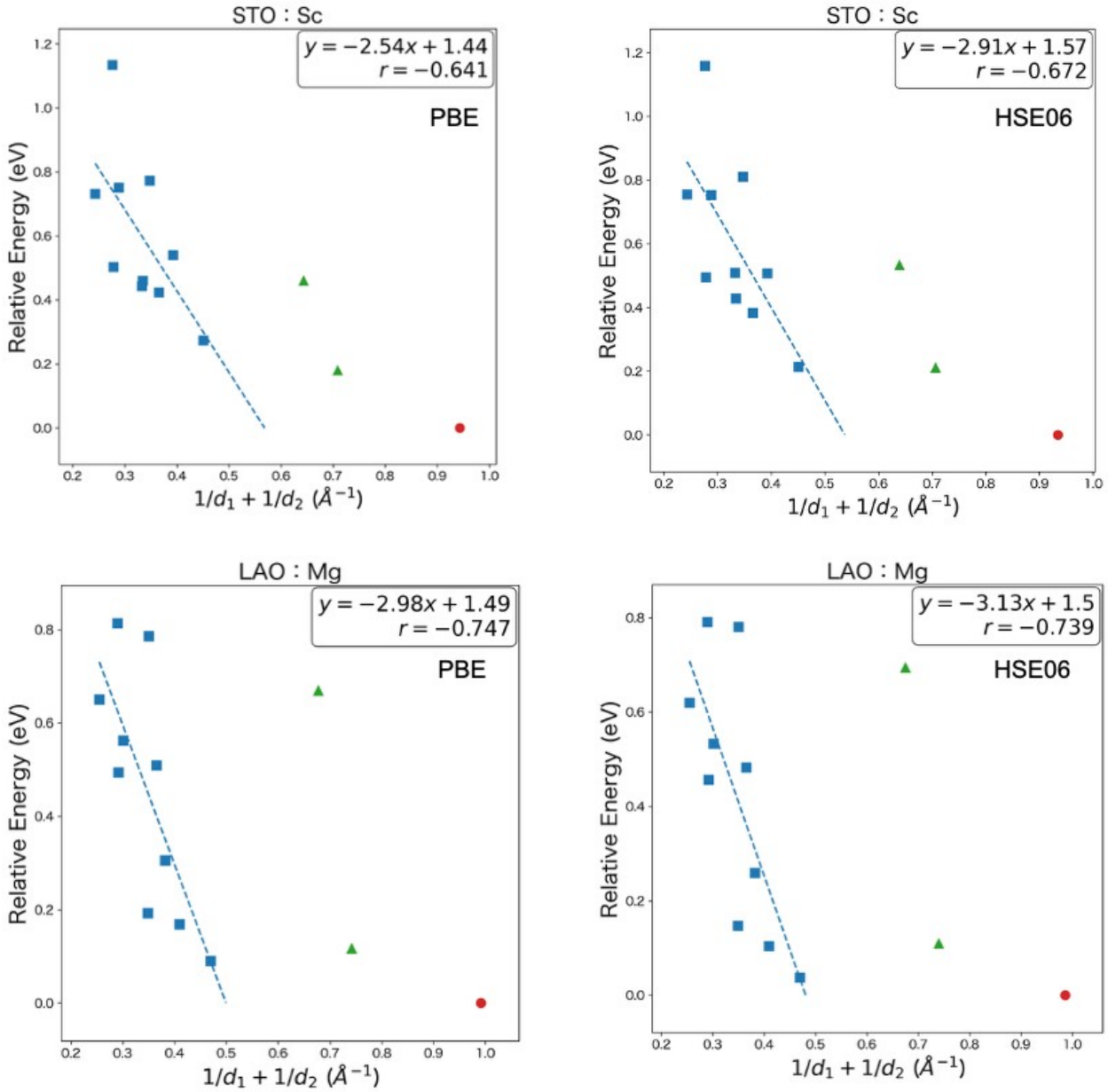
ΔE = 0.952 NN2-NN0=-0.274 ΔE = 1.46 NN2-NN0=-0.0739

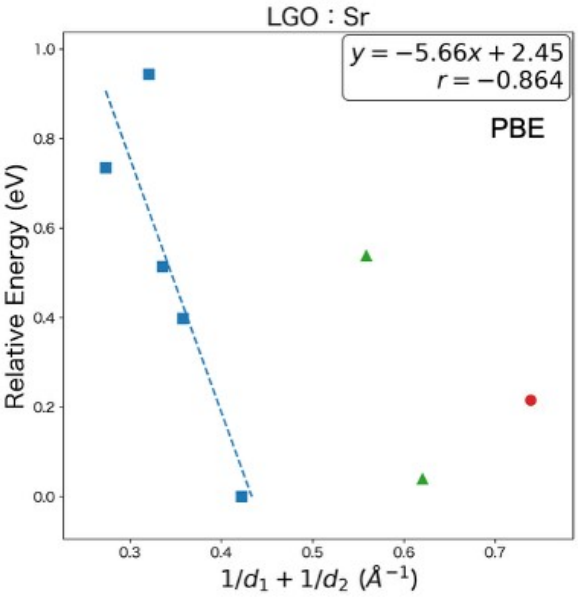


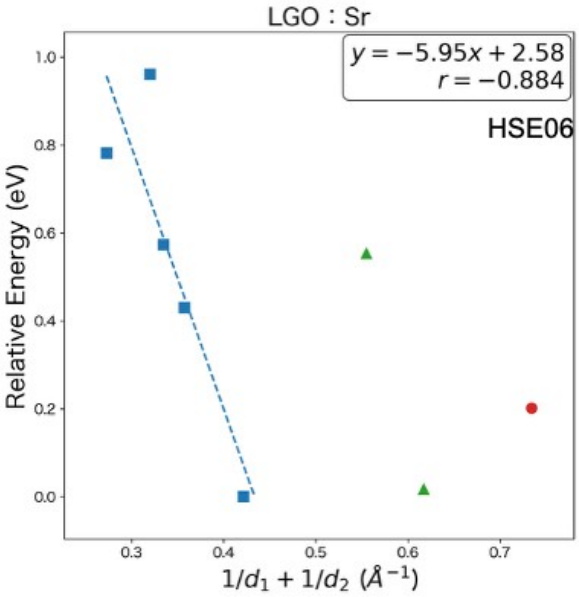
320 atoms

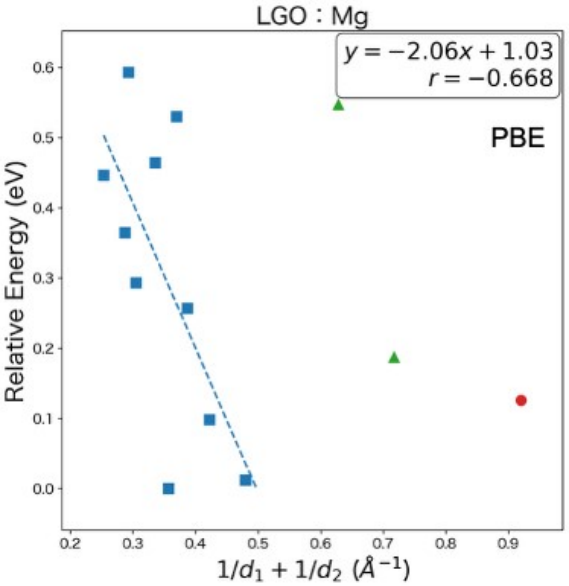
ΔE = 0.918 NN2-NN0=-0.459 ΔE = 1.28 NN2-NN0=-0.249

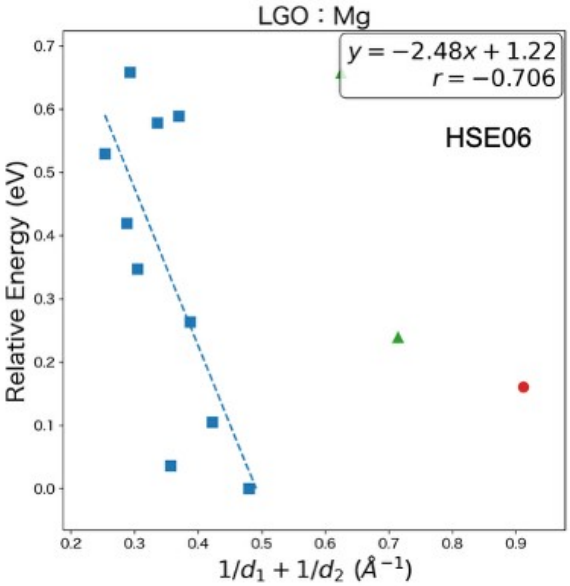
Figure S2: Comparison of trends for various lattices with 80 atoms in the supercell and between PBE (PBE+U where applicable) and HSE06.

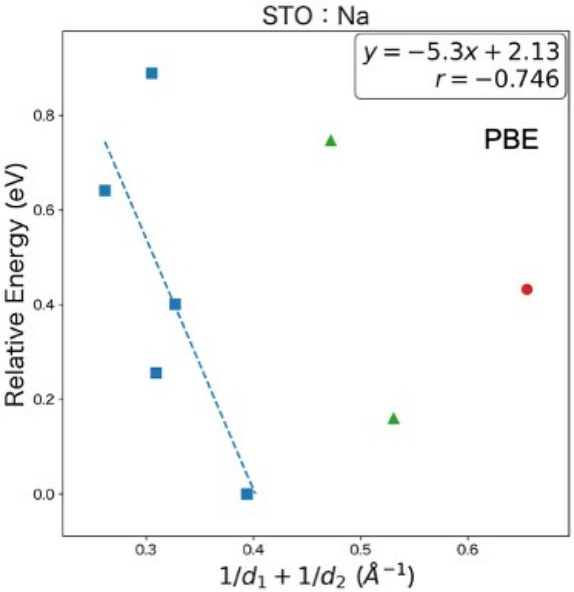


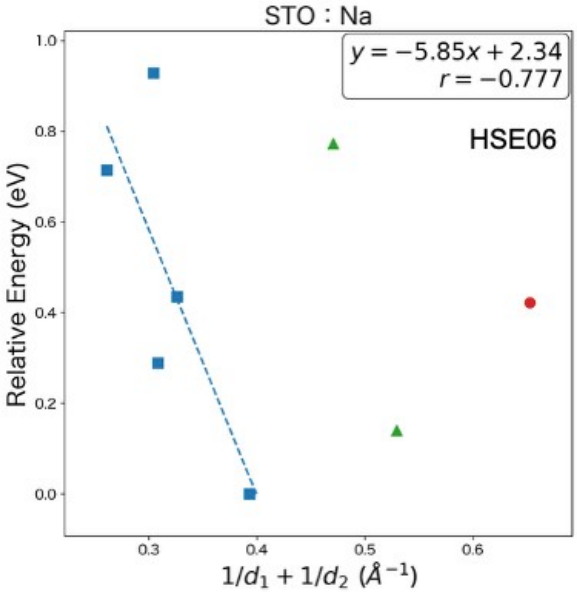

LGO : Sr
$y = -5.66x + 2.45$
$r = -0.864$
PBE
Relative Energy (eV)
$1/d_1 + 1/d_2$ ($Å^{-1}$)


LGO : Sr
$y = -5.95x + 2.58$
$r = -0.884$
HSE06
Relative Energy (eV)
$1/d_1 + 1/d_2$ ($Å^{-1}$)


LGO : Mg
$y = -2.06x + 1.03$
$r = -0.668$
PBE
Relative Energy (eV)
$1/d_1 + 1/d_2$ ($Å^{-1}$)


LGO : Mg
$y = -2.48x + 1.22$
$r = -0.706$
HSE06
Relative Energy (eV)
$1/d_1 + 1/d_2$ ($Å^{-1}$)

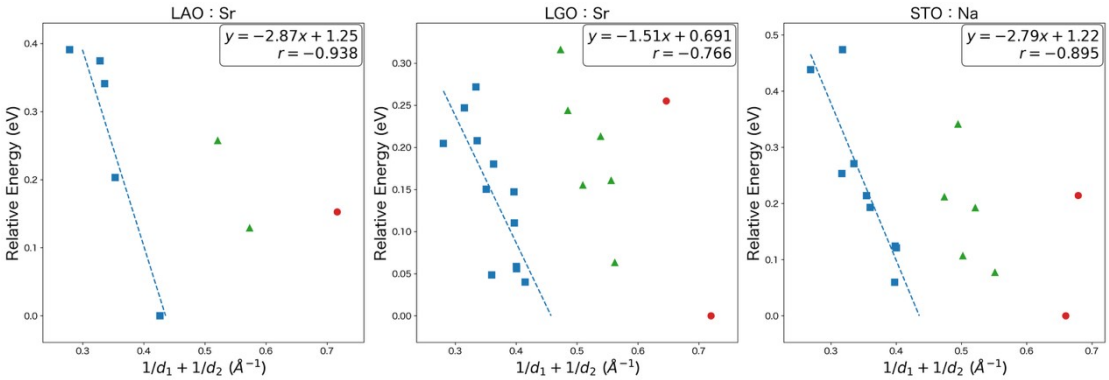

STO : Na
$y = -5.3x + 2.13$
$r = -0.746$
PBE
Relative Energy (eV)
$1/d_1 + 1/d_2$ ($Å^{-1}$)


STO : Na
$y = -5.85x + 2.34$
$r = -0.777$
HSE06
Relative Energy (eV)
$1/d_1 + 1/d_2$ ($Å^{-1}$)

0 temperature Stable Phases with 80 atoms in the supercell

Figure S3 shows the relative energies of vacancy configurations plotted as functions of the Coulomb metric for Sr- or Mg-doped $LaAlO_3$, Sr- or Mg-doped $LaGaO_3$, and Na- or Sc-doped $SrTiO_3$ in the 80-atom supercells of the 0 K stable phase. For A-site-doped LGO and STO, two distinct NN2 configurations are present, corresponding to axial and equatorial arrangements.

a



b

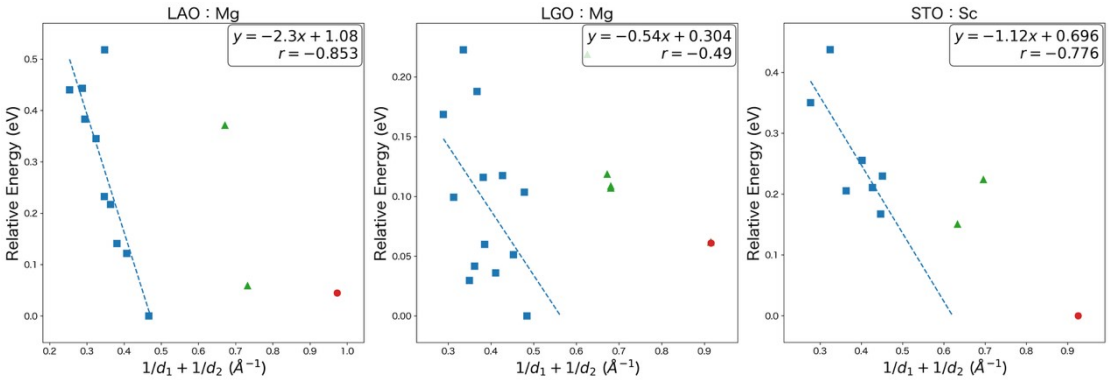


Figure S3. Relative energies of vacancy configurations plotted as functions of the Coulomb metric ($1/d_1 + 1/d_2$) for the 80-atom supercells constructed from the most stable 0 K phase. (a) A-site doping; (b) B-site doping. Blue squares, green triangles, and red circles correspond to NN0, NN1, and NN2 configurations, respectively. The dotted line represents a linear fit to the NN0 data. The fitting equation and the corresponding correlation coefficient (r) are given in the upper-right corner of each panel.

Overall, the results exhibit trends similar to those obtained for the 800 K stable phase, supporting the physical validity of the constrained structural relaxations employed in this work. For Mg-doped $LaGaO_3$, however, the linear fit for the NN0 configurations is substantially weaker ($|r| = -0.49$). We attribute this behavior primarily to the strong dependence of vacancy energies on whether the vacancy occupies an axial or equatorial position. Consistent with this interpretation, Gambino et al. reported a pronounced energy difference between axial and equatorial vacancy configurations in Mg-doped LGO.