Supplementary material for "Predicting polarization and nonlinear dielectric response of arbitrary perovskite superlattice sequences"

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In this supplementary material, we present the form of the cluster expansions for the layer polarizations of AO and TiO$_2$ layers, and give the fitted values of the effective cluster interaction coefficients for the layer polarizations and the lattice constants.

As explained in the main text, we separate the D-dependence of the layer polarization of an AO layer into an odd part $p^{(-)}_{\rm AO}(D)$ (reflecting the inversion-symmetry-conserving part of its environment) and an even part $p^{(+)}_{\rm AO}(D)$ (reflecting the inversion-symmetry-breaking character), and similarly for TiO$_2$ layers. Then our model for AO layers is

$$\begin{aligned} p^{(-)}_{\rm AO} &= \mathcal{J} + \mathcal{J}_0 s_0 + \mathcal{J}'_0 t_0 + \mathcal{J}_1(s_{\bar 1} + s_1) + \mathcal{J}'_1(t_{\bar 1} + t_1) \\ &+ \mathcal{J}_2(s_{\bar 2} + s_2) + \mathcal{J}_{01}(s_{\bar 1}s_0 + s_0 s_1) \\ &+ \mathcal{J}_{02}(s_{\bar 2}s_0 + s_0 s_2) + \mathcal{J}_{\bar 1 1}s_{\bar 1}s_1 \\ &+ \mathcal{J}_{12}(s_{\bar 2}s_{\bar 1} + s_1 s_2) \end{aligned} \tag{1}$$

and

$$\begin{aligned} p^{(+)}_{\rm AO} &= \widetilde{\mathcal{J}}_1(s_{\bar 1} - s_1) + \widetilde{\mathcal{J}}'_1(t_{\bar 1} - t_1) \\ &+ \widetilde{\mathcal{J}}_{01}(s_{\bar 1}s_0 - s_0 s_1) + \widetilde{\mathcal{J}}'_{01}(t_{\bar 1}s_0 - s_0 t_1) \\ &+ \widetilde{\mathcal{J}}'_{10}(s_{\bar 1}t_0 - t_0 s_1) + \widetilde{\mathcal{J}}_{12}(s_{\bar 2}s_{\bar 1} - s_1 s_2)\,. \end{aligned} \tag{2}$$

Eq. (1) is equivalent to Eq. (2) of the main text, except that here we introduce the condensed notation $t_j = s_j^2$. The layers are labeled according to the sequence $[\cdots \bar 3.\bar 2.\bar 1.0.1.2.3 \cdots]$ where numbers represent AO layers, periods represent TiO$_2$ layers, and the central AO layer 0 is the one whose layer polarization is being expanded. The coefficients $\mathcal{J}(D)$, $\mathcal{J}_0(D)$, ... are odd functions of D; the $\widetilde{\mathcal{J}}_1(D)$, $\widetilde{\mathcal{J}}'_1(D)$, ... are even functions of D; and the combinations of spins appearing in Eqs. (1-2) are the symmetry-appropriate ones. The D-dependence of the coefficients has been suppressed for simplicity of notation.

The corresponding expansion for the layer polarization of a TiO$_2$ layer is

$$\begin{aligned} p^{(-)}_{\rm TiO_2} &= \mathcal{K} + \mathcal{K}_1(s_{\bar 1} + s_1) + \mathcal{K}'_1(t_{\bar 2} + t_2) + \mathcal{K}_2(s_{\bar 2} + s_2) \\ &+ \mathcal{K}'_2(t_{\bar 1} + t_1) + \mathcal{K}_{12}(s_{\bar 2}s_{\bar 1} + s_1 s_2) + \mathcal{K}_{\bar 1 1}s_{\bar 1}s_1 \\ &+ \mathcal{K}_{\bar 2 1}(s_{\bar 2}s_1 + s_{\bar 1}s_2) \end{aligned} \tag{3}$$

and

$$\begin{aligned} p^{(+)}_{\rm TiO_2} &= \widetilde{\mathcal{K}}_1(s_{\bar 1} - s_1) + \widetilde{\mathcal{K}}'_1(t_{\bar 2} - t_2) + \widetilde{\mathcal{K}}_2(s_{\bar 2} - s_2) \\ &+ \widetilde{\mathcal{K}}_{12}(s_{\bar 2}s_{\bar 1} - s_1 s_2) + \widetilde{\mathcal{K}}'_{12}(s_{\bar 1}t_{\bar 2} - t_2 s_1) \\ &+ \widetilde{\mathcal{K}}'_{21}(s_{\bar 2}t_{\bar 1} - t_1 s_2) + \widetilde{\mathcal{K}}'_{\bar 1 1}(s_{\bar 1}t_1 - t_{\bar 1}s_1) \\ &+ \widetilde{\mathcal{K}}'_{\bar 1 2}(s_{\bar 1}t_2 - t_2 s_{\bar 1}) + \widetilde{\mathcal{K}}_{\bar 2 1}(s_{\bar 2}s_1 - s_{\bar 1}s_2) \\ &+ \widetilde{\mathcal{K}}'_{\bar 2 1}(s_{\bar 2}t_1 - t_{\bar 1}s_2)\,, \end{aligned} \tag{4}$$

where $\mathcal{K}$ and $\widetilde{\mathcal{K}}$ coefficients are odd and even in D respectively. Here the labeling scheme is $[\cdots \bar 3.\bar 2.\bar 1.1.2.3 \cdots]$ with the central TiO$_2$ layer being the one whose layer polarization is being expanded.

The parameters $\mathcal{J}(D)$, $\widetilde{\mathcal{J}}(D)$, $\mathcal{K}(D)$, and $\widetilde{\mathcal{K}}(D)$ are expressed as fifth-order Taylor expansions in D, with the Taylor coefficients obtained from a least-squares fitting to the first-principles calculations of $p_j(D)$ for superlattices in the database. Also, recall that the supercell lattice constant $c(D)$ was expanded in terms of parameters $\mathcal{C}_q(D)$ ($q = 1, ..., 4$) as specified in Eq. (3) of the main text. The $\mathcal{C}(D)$ were similarly fitted to the database, but now as fourth-order Taylor expansions in D.

The fitted parameter values are given in the following tables.

Tables

TABLE I: Fitted first-, third-, and fifth-order-in-D Taylor coefficients of effective cluster interactions for $p^{(-)}_{\mathrm{AO}}(D)$ in Eq. (1), and zeroth-, second-, and fourth-order-in-D Taylor coefficients of effective cluster interactions for $p^{(+)}_{\mathrm{AO}}(D)$ in Eq. (2).

	$\mathcal{J}$	$\mathcal{J}_0$	$\mathcal{J}'_0$	$\mathcal{J}_1$	$\mathcal{J}'_1$	$\mathcal{J}_2$	$\mathcal{J}_{01}$	$\mathcal{J}_{02}$	$\mathcal{J}_{\bar{1}1}$	$\mathcal{J}_{12}$
1st	2.2771	0.1113	0.0819	0.0034	0.0007	−0.0018	0.0197	0.0031	0.0026	0.0013
3rd	−0.0459	−0.2090	−0.0319	−0.0513	−0.0129	−0.0078	−0.0512	−0.0211	−0.0149	−0.0064
5th	0.2793	0.3690	0.1236	0.1287	0.0533	0.0293	0.0554	0.0339	0.0071	0.0209

	$\widetilde{\mathcal{J}}_1$	$\widetilde{\mathcal{J}}'_1$	$\widetilde{\mathcal{J}}_{01}$	$\widetilde{\mathcal{J}}'_{01}$	$\widetilde{\mathcal{J}}'_{10}$	$\widetilde{\mathcal{J}}_{12}$
0th	−0.0210	−0.0044	−0.0015	0.0001	−0.0002	−0.0005
2nd	0.0657	0.0014	0.0047	0.0037	0.0029	−0.0017
4th	−0.0569	−0.0035	0.0010	−0.0139	−0.0164	0.0081

TABLE II: Fitted first-, third-, and fifth-order-in-D Taylor coefficients of effective cluster interactions for $p^{(-)}_{\mathrm{TiO_2}}(D)$ in Eq. (3), and zeroth-, second-, and fourth-order Taylor coefficients of effective cluster interactions for $p^{(+)}_{\mathrm{TiO_2}}(D)$ in Eq. (4).

	$\mathcal{K}$	$\mathcal{K}_1$	$\mathcal{K}'_1$	$\mathcal{K}_2$	$\mathcal{K}'_2$	$\mathcal{K}_{12}$	$\mathcal{K}_{\bar{1}1}$	$\mathcal{K}_{\bar{2}1}$
1st	1.5292	−0.0097	−0.0060	0.0075	−0.0013	−0.0076	0.0033	−0.0018
3rd	0.0415	0.1203	0.0376	0.0035	0.0074	0.0148	0.0025	0.0091
5th	−0.0468	−0.1727	−0.0702	−0.0421	−0.0068	−0.0084	−0.0095	−0.0219

	$\widetilde{\mathcal{K}}_1$	$\widetilde{\mathcal{K}}'_1$	$\widetilde{\mathcal{K}}_2$	$\widetilde{\mathcal{K}}_{12}$	$\widetilde{\mathcal{K}}'_{12}$	$\widetilde{\mathcal{K}}'_{21}$	$\widetilde{\mathcal{K}}'_{\bar{1}1}$	$\widetilde{\mathcal{K}}'_{\bar{1}2}$	$\widetilde{\mathcal{K}}_{\bar{2}1}$	$\widetilde{\mathcal{K}}'_{\bar{2}1}$
0th	0.0634	−0.0057	0.0027	0.0023	0.0004	0.0001	0.0010	−0.0001	−0.0003	0.0000
2nd	−0.1468	0.0101	−0.0200	0.0106	−0.0057	−0.0169	0.0089	−0.0018	0.0014	0.0063
4th	0.0522	0.0059	0.0045	−0.0470	0.0247	0.0679	−0.0447	0.0147	−0.0030	−0.0372

TABLE III: Fitted zeroth-, second-, and fourth-order-in-D Taylor coefficients of effective cluster interactions for $c(D)$ in Eq. (3) of main text.

	$\mathcal{C}_1$	$\mathcal{C}_2$	$\mathcal{C}_3$	$\mathcal{C}_4$
0th	7.2305	0.1968	0.0543	0.0097
2nd	0.4430	0.3293	0.1675	0.0832
4th	−0.1926	−0.6367	−0.1546	−0.3744