

Supplementary Information for  
“Electronic transport in quantum-dot-in-perovskite solids”

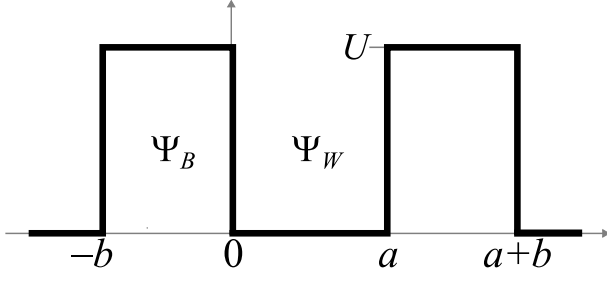
August 1, 2022

**Contents**

<b>S1 Kronig-Penney model in the effective-mass approximation</b>	<b>2</b>
<b>S2 Analytical expression for the width of the lowest subband of the Kronig-Penney model</b>	<b>2</b>
<b>S3 Kronig-Penney model beyond the effective-mass approximation: Kane model of coupled valence and conduction bands</b>	<b>3</b>
<b>S4 Material parameters for the Kronig-Penney model</b>	<b>5</b>
<b>S5 Simple model of the electrostatic shift from the halogen ligands</b>	<b>6</b>

## S1 Kronig-Penney model in the effective-mass approximation

We follow the derivation and notation of Grundmann,<sup>1</sup> whose approach is closely based on Kronig and Penney's original solution.<sup>2</sup> We generalize the solution to allow for different effective masses in the square well and barrier.



Consider the periodic square well potential above. The wavefunctions in the well ( $0 \leq x \leq a$ ) are oscillatory with wavenumber  $K$ , while in the barrier ( $-b \leq x \leq 0$ ) they are exponential with wavenumber  $\kappa$ ,

$$\Psi_W(x) = Ae^{iKx} + Be^{-iKx} \quad (1)$$

$$\Psi_B(x) = Ce^{\kappa x} + De^{-\kappa x}. \quad (2)$$

We apply the usual boundary conditions requiring that the wavefunction and its derivative (more generally the probability current  $\Psi'(x)/m^*$  where  $m^*$  is the effective mass) are continuous at the boundaries  $x = 0$  and  $x = a$ . To obtain  $\Psi_B(a)$  and  $\Psi_B'(a)$  we use Bloch's theorem  $\Psi(x+P) = e^{ikP}\Psi(x)$  where  $k$  is the crystal wavenumber and  $P = a+b$  is the period. This yields<sup>†</sup>

$$A + B = C + D \quad (3)$$

$$(1/m_W)(iKA - iKB) = (1/m_B)(\kappa C - \kappa D) \quad (4)$$

$$Ae^{iKa} + Be^{-iKa} = e^{ik(a+b)}(Ce^{-\kappa b} + De^{\kappa b}) \quad (5)$$

$$(1/m_W)(iAKe^{iKa} - iKBe^{-iKa}) = (1/m_B)e^{ik(a+b)}(\kappa Ce^{-\kappa b} - \kappa De^{\kappa b}). \quad (6)$$

A solution exists only if the matrix of coefficients has determinant zero. This condition leads to an implicit equation for the energy  $E$  as a function of the wavenumber  $k$ ,

$$\cos k(a+b) = \mathcal{A}(E), \quad (7)$$

where we have defined  $\mathcal{A}(E)$  as the generalization of the function  $\mathcal{B}(E)$  in Ref. 1 to the case of different effective masses,

$$\mathcal{A}(E) = \cos aK \cosh b\kappa - \sin aK \sinh b\kappa \left( \frac{Km_B}{2\kappa m_W} - \frac{\kappa m_W}{2Km_B} \right). \quad (8)$$

The energy dependence of  $\mathcal{A}(E)$  arises from the dispersion relations relating  $K$  and  $\kappa$  to the energy  $E$ . In the next section we discuss two choices for these: parabolic dispersion and the more accurate dispersion given by the two-band Kane model.<sup>3</sup> The effective masses  $m_W$  and  $m_B$  in the well and barrier, respectively, are constants in the case of parabolic dispersion but depend on energy within the Kane model. The Kronig-Penney band structure  $E(k)$  is obtained implicitly by choosing a value of  $k$  and then numerically solving Eq. 8 for  $E$ . Multiple solutions exist for each value of  $k$  and correspond to different subbands. The extrema of these subbands occur at  $k = 0$  and  $k = \pi/(a+b)$  and thus the width  $W$  of the lowest subband is given by the difference  $\Delta E$  between the first roots satisfying  $\mathcal{A}(E) = \pm 1$ .

## S2 Analytical expression for the width of the lowest subband of the Kronig-Penney model

In the Kronig-Penney model, the extrema  $E_i$  of the band structure  $E(k)$  can be found by solving the equation

$$\mathcal{A}(E) = \cos aK \cosh b\kappa - \sin aK \sinh b\kappa \left( \frac{Km_B}{2\kappa m_W} - \frac{\kappa m_W}{2Km_B} \right) = \pm 1 \quad (9)$$

where  $a$ ,  $m_W$ ,  $K$  and  $b$ ,  $m_B$ ,  $\kappa$  are the width, effective mass, and wavenumber for the quantum well and barrier, respectively. This expression depends on the energy  $E$  through the dispersion relations assumed in each region. Our derivation of the superlattice bandwidth does not depend on these relations but we will give results for specific choices at the end of this section. Each Kronig-Penney band has two extrema and thus the width of the lowest-lying band is the difference of the first two roots,  $W = E_2 - E_1$ . In the following we develop an analytical expression for  $W$  valid in the limit of large  $U$ .

We begin by defining a characteristic energy associated with the barrier,  $U_0 = \hbar^2/2m_B b^2$ . When the barrier  $U$  is large compared to both  $E$  and  $U_0$ , the cosh and sinh terms in Eq. 9 can be approximated by simple exponentials. This leads to a decaying oscillatory function that accurately approximates  $\mathcal{A}(E)$  in the limit of large  $U$ ,

$$\tilde{\mathcal{A}}(E) = \frac{1}{2}e^{(U/U_0)^{1/2}} \left[ \cos aK + \frac{1}{2} \left( \frac{a}{b} \right) \left( \frac{m_W}{m_B} \right) \left( \frac{U}{U_0} \right)^{1/2} \frac{\sin aK}{aK} \right], \quad (10)$$

<sup>†</sup>Equations 5 and 6 fix several misprints in Eqs. 6.11c and 6.11d of Ref. 1

To obtain  $W$  we linearize  $\tilde{A}(E)$  around its first zero. This root can be easily found when  $U$  is large because the cosine term is negligible and thus the desired root  $E_0$  is given by the condition  $aK = \pi$ .

To perform the linearization we simply evaluate the derivative  $d\tilde{A}(E)/dE$  at  $E_0$ . The approximate Kronig-Penney bandwidth  $\tilde{W}$  is then given by two times the reciprocal of this derivative. The result is

$$\tilde{W} = e^{-(U/U_0)^{1/2}} W_0, \quad (11)$$

where

$$W_0 = 4\sqrt{2} \left( \frac{m_B}{m_W} \right) \left( \frac{K}{K'} \right) \left( \frac{\hbar^2/m_B a^2}{U} \right)^{1/2} \quad (12)$$

and the prime denotes the derivative with respect to energy. Equations 11 and 12 give the most general expression for the superlattice bandwidth. If specific dispersion relations are assumed then a more explicit expression can be obtained. Here we give two examples that correspond to the assumptions of the main paper.

We first assume standard parabolic dispersion,  $\hbar K = [2m_W^0 E]^{1/2}$  in the well region and  $\hbar \kappa = [2m_B^0 (U - E)]^{1/2}$  in the barrier region. The root  $E_0$  is then simply the energy of the lowest bound state of the infinite square well,  $E_0 = \hbar^2 \pi^2 / 2m_W^0 a^2$ . By evaluating Eq. 12 at this energy we obtain the explicit expression

$$W_0 = 8\sqrt{2} \left( \frac{m_B^0}{m_W^0} \right) \left( \frac{\hbar^2 \pi^2}{m_W^0 a^2} \right) \left( \frac{\hbar^2 / m_B^0 a^2}{U} \right)^{1/2} \quad (13)$$

Alternatively, we can adopt a more realistic dispersion relation for the PbS well. The bands near the fundamental gap at the L point can be accurately parameterized by a two-band Kane model defined by the Kane energy  $E_p$  (see Section S3 for details). This model leads to an energy-dependent effective mass  $m_W = m_W^0 (1 + 3mE/m_W^0 E_p)$  and a more complicated dispersion  $\hbar K = [2m_W E]^{1/2}$ . The band structure is parabolic at the zone center and then becomes asymptotically linear with constant band velocity  $v$  given by  $E_p = 6mv^2$ . The root  $E_0$  now takes the form

$$E_0 = \left( \frac{m_W^0}{m} \right) E_p \left[ (1 + 6\hbar^2 \pi^2 m / (m_W^0)^2 a^2 E_p)^{1/2} - 1 \right] / 6, \quad (14)$$

By evaluating Eq. 12 at this energy we obtain the expression

$$W_0 = 8\sqrt{2} \left( \frac{m_B^0}{m} \right) \left( \frac{E_p}{3} \right) \left[ 1 - \left( 1 + \frac{6\hbar^2 \pi^2 m}{(m_W^0)^2 a^2 E_p} \right)^{-1/2} \right] \left( \frac{\hbar^2 / m_B^0 a^2}{U} \right)^{1/2}. \quad (15)$$

In the limit of large Kane energy  $E_p$ , these expressions for  $E_0$  and  $W_0$  correctly reduce to the parabolic results.

To summarize, our expressions show that the Kronig-Penney bandwidth  $W$  decays approximately exponentially with the square root of the height of the potential barrier. All the other physical parameters appear in a prefactor that varies more slowly. The detailed form of this prefactor is determined by the dispersion relations.

### S3 Kronig-Penney model beyond the effective-mass approximation: Kane model of coupled valence and conduction bands

The Kane model for the coupled valence and conduction bands of a single material is defined by the Hamiltonian

$$H(k) = \begin{pmatrix} E_c & -i\hbar \frac{kP}{m\sqrt{3}} \\ i\hbar \frac{kP}{m\sqrt{3}} & E_v \end{pmatrix}. \quad (16)$$

The Kane momentum matrix element  $P = -i\langle s|\hat{P}|Z\rangle$  is related to the Kane energy  $E_p = 2|P|^2/m$  where  $m$  is the mass of a free electron. Our numerical values for  $E_p$  are given in Section S4. We diagonalize this matrix to obtain

$$(E_c - E)(E_v - E) = \frac{1}{3} \frac{\hbar^2}{m^2} P^2 k^2 = \frac{E_p}{3} \frac{\hbar^2}{2m} k^2. \quad (17)$$

Equation 17 is quadratic in  $E$  and so there are two eigenvalues  $E_{\pm}(k)$  which are symmetric about the midpoint of the band gap  $(E_v + E_c)/2$  and with extrema at  $E_c$  and  $E_v$ , respectively. We select the upper eigenvalue and drop the  $+$  subscript to write the dispersion relation as

$$E(k) = E_c + \frac{1}{2} E_g \left( \sqrt{1 + 2\hbar^2 k^2 / E_g m^*} - 1 \right) \quad (18)$$

where the band-edge mass  $m^*$  is related to the band gap and Kane energy by  $m^* = 3mE_g/E_p$ .

We now turn to the Kronig-Penney model and use the above Hamiltonian to describe both the PbS quantum well and the CsPbI<sub>3</sub> barrier. In the PbS quantum well ( $W$ ) the Hamiltonian depends on the wavenumber  $K$  inside the well,

$$H^W(K) = \begin{pmatrix} E_c^W & -i\hbar \frac{KP^W}{m\sqrt{3}} \\ i\hbar \frac{KP^W}{m\sqrt{3}} & E_v^W \end{pmatrix}. \quad (19)$$

The upper band has the dispersion relation

$$E^W(K) = E_c^W + \frac{1}{2}E_g^W \left( \sqrt{1 + 2\hbar^2 K^2 / E_g^W m_w^0} - 1 \right) \quad (20)$$

where the band-edge mass  $m_w^0$  is given by  $m_w^0 = 3mE_g^W / E_p^W$ . The corresponding eigenvector is

$$\mathbf{v} = \begin{pmatrix} 1 \\ \Theta^W(K) \end{pmatrix} \quad (21)$$

where for convenience we have defined

$$\Theta^W(K) = i\hbar \frac{KP^W}{m\sqrt{3}} \frac{1}{E^W(K) - E_v^W}. \quad (22)$$

The wave function in the quantum well can therefore be written

$$\Psi_W(x) = Ae^{iKx} \begin{pmatrix} 1 \\ \Theta^W(K) \end{pmatrix} + Be^{-iKx} \begin{pmatrix} 1 \\ -\Theta^W(K) \end{pmatrix} \quad (23)$$

which is analogous to Eq. 1 in Section S1. In the CsPbI<sub>3</sub> barrier ( $B$ ) the Hamiltonian  $H^B(\kappa)$  has the same form as Eq. 19 and thus the wavefunction can be written as

$$\Psi_B(x) = Ce^{\kappa x} \begin{pmatrix} 1 \\ -i\Theta^B(\kappa) \end{pmatrix} + De^{-\kappa x} \begin{pmatrix} 1 \\ i\Theta^B(\kappa) \end{pmatrix} \quad (24)$$

which is analogous to Eq. 2 in Section S1 and where for convenience we have defined

$$\Theta^B(\kappa) = i\hbar \frac{\kappa P^B}{m\sqrt{3}} \frac{1}{E^B(\kappa) - E_v^B}. \quad (25)$$

We now apply the boundary conditions for the Kronig-Penney model. In Ref. 4 we showed that continuity of the probability flux density across the boundary  $x = 0$  requires that

$$\begin{pmatrix} \Psi_W^c(0) \\ P^W \Psi_W^v(0) \end{pmatrix} = T_{tr} \begin{pmatrix} \Psi_B^c(0) \\ P^B \Psi_B^v(0) \end{pmatrix} \quad (26)$$

where  $c$  and  $v$  denote the conduction and valence components and  $T_{tr}$  is a  $2 \times 2$  matrix with determinant 1. We will set  $T_{tr}$  to the unit matrix. Equation 26 then becomes

$$\begin{pmatrix} A + B \\ P^W(A - B)\Theta^W(K) \end{pmatrix} = \begin{pmatrix} C + D \\ -iP^B(C - D)\Theta^B(\kappa) \end{pmatrix} \quad (27)$$

A second pair of equations is obtained for the boundary  $x = a$  using Bloch's theorem. We collect all four equations into a form analogous to Eqs. 3–6 in Section S1:

$$A + B = C + D \quad (28)$$

$$P^W(A - B)\Theta^W(K) = -iP^B(C - D)\Theta^B(\kappa) \quad (29)$$

$$Ae^{iKa} + Be^{-iKa} = e^{ik(a+b)}(Ce^{-\kappa b} + De^{\kappa b}) \quad (30)$$

$$P^W \Theta^W(K)(Ae^{iKa} - Be^{-iKa}) = ie^{ik(a+b)}P^B \Theta^B(\kappa)(-Ce^{-\kappa b} + De^{\kappa b}) \quad (31)$$

A solution exists only if the matrix of coefficients has determinant zero. This condition leads to an implicit equation for the energy  $E$  as a function of the wavenumber  $k$ ,

$$\cos k(a+b) = \mathbb{A}(E), \quad (32)$$

where  $\mathbb{A}(E)$  has a form analogous to  $\mathcal{A}(E)$  from Section S1,

$$\mathbb{A}(E) = \cos aK \cosh b\kappa - \sin aK \sinh b\kappa \left( \frac{P^W \Theta^W(K)}{2P^B \Theta^B(\kappa)} - \frac{P^B \Theta^B(\kappa)}{2P^W \Theta^W(K)} \right). \quad (33)$$

Using the Kane energies  $E_p^W = (P^W)^2/m$  and  $E_p^B = (P^B)^2/m$  it is easy show that Eq. 33 can be written equivalently as

$$\mathbb{A}(E) = \cos aK \cosh b\kappa - \sin aK \sinh b\kappa \left( \frac{Km_B}{2\kappa m_W} - \frac{\kappa m_W}{2Km_B} \right) \quad (34)$$

where the masses are now the energy-dependent effective masses  $m_W = m_w^0(1 + 3mE/m_w^0 E_p^W)$  plus an analogous expression for  $m_B$ . Equations 8 and 34 are identical which establishes that solving the Kronig-Penney model using the Kane model leads to the same result as the standard solution with energy-dependent masses in the well and barrier.

#### S4 Material parameters for the Kronig-Penney model

We used the following values for the material parameters of the PbS well ( $W$ ) and CsPbI<sub>3</sub> barrier ( $B$ ) in the Kronig-Penney model.

Parameter	PbS ( $W$ )	Ref.	CsPbI <sub>3</sub> ( $B$ )	Ref.
Band gap, $E_g$ (eV)	0.41	5	1.84	6
Band-edge mass, $m^0$ ( $m$ )	0.09	3	0.32	6
Kane energy, $E_p$ (eV)	13.7	3	17.39	6

## S5 Simple model of the electrostatic shift from the halogen ligands

Consider a layer of halogen atoms adsorbed on PbS(100) at a distance  $h$  from the surface. Assume each halogen accepts 1 electron from the PbS. We approximate the resulting charge distribution as being completely localized along the surface normal and uniformly smeared out in the plane, exactly like a textbook parallel-plate capacitor. This creates a uniform electric field  $\mathcal{E}(x)$  between the surface and the halogen layer that depends only on the coverage  $x$  of halogens per unit area. The electrostatic shift due to this dipole layer of thickness  $h$  is simply  $\Delta V(x) = eh\mathcal{E}(x)$ . Below we derive a simple expression for  $\mathcal{E}(x)$ .

There are two contributions to  $\mathcal{E}(x)$ . The first is from the charge transfer mentioned above and is proportional to the halogen coverage and therefore can be written  $Ax$  where  $A$  is a single constant for all the halogens.

The second contribution arises from the polarization of the halogen atoms due to the electric field they experience. This contribution is proportional to three quantities: the atomic polarizability  $\alpha$  of the halogen, the coverage  $x$ , and the electric field. It can therefore be written  $B\alpha x\mathcal{E}(x)$  where  $B$  is a constant for all halogens.

Putting these two contributions together we find that  $\mathcal{E}(x) = Ax - B\alpha x\mathcal{E}(x)$ , which can be easily solved for the electric field:

$$\mathcal{E}(x) = \frac{Ax}{1 + B\alpha x}. \quad (35)$$

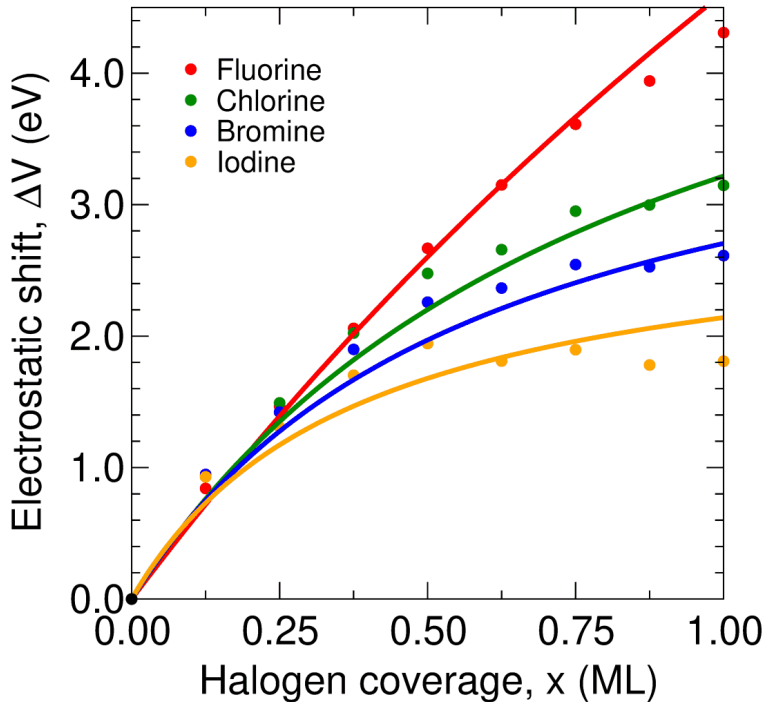
The electrostatic shift is therefore

$$\Delta V(x) = \frac{ehAx}{1 + B\alpha x}. \quad (36)$$

This expression describes the DFT results from Fig. 3(b) very well, as shown by the solid curves and symbols below, respectively. The constants  $A$  and  $B$  can be written in terms of various fundamental constants but were here treated as fitting parameters for simplicity. The values of  $h$  were obtained from our DFT calculations and the values of  $\alpha$  are from Ref. 7 as tabulated below.

As discussed in the main text, this model explains the behavior of the DFT results at both low and high halogen coverage. At small values of  $x$ , Eq. 36 shows that  $\Delta V(x)$  is linearly proportional to  $x$  with a coefficient  $h$  (which varies modestly with the halogen). For large values of  $x$ ,  $\Delta V(x)$  saturates at a constant whose value is proportional to  $h/\alpha$  (which varies strongly with the halogen).

Parameter	F	Cl	Br	I
Distance, $h$ (Å)	2.33	2.69	2.83	3.12
Polarizability, $\alpha$ (a.u.)	3.75	14.6	21.0	32.9



## References

- [1] M. Grundmann, *The Physics of Semiconductors: An Introduction Including Devices and Nanophysics*, Springer, 2010.
- [2] R. de L. Kronig and W. G. Penney, *Proceedings of the Royal Society A: Mathematical, Physical and Engineering Sciences*, 1931, **130**, 499–513.
- [3] E. A. Gaulding, X. Chen, Y. Yang, S. P. Harvey, B. To, Y. H. Kim, M. C. Beard, P. C. Sercel and J. M. Luther, *ACS Materials Letters*, 2020, **2**, 1464–1472.
- [4] A. V. Rodina, A. Y. Alekseev, Al. L. Efros, M. Rosen and B. K. Meyer, *Physical Review B*, 2002, **65**, 125302.
- [5] I. Kang and F. W. Wise, *J. Am. Optical Soc. B*, 1997, **14**, 1632–1646.
- [6] Q. Zhao, A. Hazarika, L. T. Schelhas, J. Liu, E. A. Gaulding, G. Li, M. Zhang, M. F. Toney, P. C. Sercel, and J. M. Luther, *ACS Energy Lett.*, 2020, **5**, 238–247.
- [7] P. Schwerdtfeger and J. K. Nagle, *Molecular Physics*, 2019, **117**, 1200–1225.