Supplementary Materials for

"Accurate Determination of Formation and Ionization Energies of Charged Defects in Two-Dimensional Materials"

Analytic expression for the asymptotic behavior of $IE(L_s, L_z)$.

The strategy we adopt to arrive at the asymptotic form of the ionization energy presented in Eq. (4) of the manuscript is to first write down a general expression (S1) for the ionization energy which is valid for all $L_s(= L_x = L_y)$ and L_z. We formally expand the ionization energy $IE(L_s, L_z)$ in the two variables, L_s and L_z, as follows:

$$\begin{aligned} IE(L_s, L_z) &= \sum_{i,j=-\infty}^{\infty} c_{i,j} L_s^i L_z^j \\ &= \cdots + \frac{1}{L_z^2}\left(\cdots + \frac{c_{-2,-2}}{L_s^2} + \frac{c_{-1,-2}}{L_s} + c_{0,-2} + c_{1,-2}L_s + c_{2,-2}L_s^2 + \cdots\right) \\ &+ \frac{1}{L_z}\left(\cdots + \frac{c_{-2,-1}}{L_s^2} + \frac{c_{-1,-1}}{L_s} + c_{0,-1} + c_{1,-1}L_s + c_{2,-1}L_s^2 + \cdots\right) \\ &+ \left(\cdots + \frac{c_{-2,0}}{L_s^2} + \frac{c_{-1,0}}{L_s} + c_{0,0} + c_{1,0}L_s + c_{2,0}L_s^2 + \cdots\right) \\ &+ L_z\left(\cdots + \frac{c_{-2,1}}{L_s^2} + \frac{c_{-1,1}}{L_s} + c_{0,1} + c_{1,1}L_s + c_{2,1}L_s^2 + \cdots\right) \\ &+ L_z^2\left(\cdots + \frac{c_{-2,2}}{L_s^2} + \frac{c_{-1,2}}{L_s} + c_{0,2} + c_{1,2}L_s + c_{2,2}L_s^2 + \cdots\right) \\ &+ \cdots \end{aligned} \tag{S1}$$

Then, in order to identify which of the constants of the expansion are non-zero, we take three separate physical limits for which the functional dependence of the electrostatic energy is known: (1) $fixed\ L_s, L_z \to \infty$, (2) $fixed\ L_z, L_s \to \infty$, and (3) $L_s = L_z = L \to \infty$. This greatly simplifies the expansion, which we then approximate for the presented case of $L_z \gg L_s \gg 0$.

Limit (1): $L_z \to \infty$ at a fixed L_s. As depicted in Fig. S1 (a), when $L_z \gg L_s$ the charge variations within the plane become a minor part of the total energy, and the total energy is dominated by the approximate problem of a uniformly charged sheet in a compensating background. In this case, we can find the total energy by simple integration of $\frac{\sqrt{3}\epsilon_0}{4}\int_{-L_z/2}^{L_z/2}\int_{-L_y/2}^{L_y/2}\int_{-L_x/2}^{L_x/2}|\boldsymbol{E}|^2 dxdydz$, where $\boldsymbol{E}$ is the electric field and $|\boldsymbol{E}| = \frac{q}{\sqrt{3}L_s^2\epsilon_0}\left(1 - \frac{2}{L_z}|z|\right)$, to arrive at $E_{tot} = \frac{q^2}{12\sqrt{3}L_s^2\epsilon_0}L_z = \frac{\beta' L_z}{L_s^2}\left(= \frac{q^2}{24S\epsilon_0}L_z = \frac{\beta L_z}{S}\right)$. This linear divergence of the charged system directly leads to a divergent ionization energy IE with increasing L_z. Explicitly, we can write the ionization energy in this limit as $IE(L_s, L_z) = \frac{\beta' L_z}{L_s^2} + g(L_s, L_z)$, where $g(L_s, L_z)$ is the remaining part of the ionization energy which is non-divergent in L_z. When compared with Eq. (S1), we see that all the coefficients that contain L_z^2 or higher order must vanish from the expansion. In other words, $c_{i,j} = 0$ for $(j > 1)$ and $c_{i,1} = 0$ for $i \neq -2$ with $c_{-2,1} = \beta'$. This reduces Eq. (S1) to

$$IE(L_s, L_z) = \cdots + \frac{1}{L_z^2}\left(\cdots + \frac{c_{-2,-2}}{L_s^2} + \frac{c_{-1,-2}}{L_s} + c_{0,-2} + c_{1,-2}L_s + c_{2,-2}L_s^2 + \cdots\right)$$
$$+ \frac{1}{L_z}\left(\cdots + \frac{c_{-2,-1}}{L_s^2} + \frac{c_{-1,-1}}{L_s} + c_{0,-1} + c_{1,-1}L_s + c_{2,-1}L_s^2 + \cdots\right)$$
$$+ \left(\cdots + \frac{c_{-2,0}}{L_s^2} + \frac{c_{-1,0}}{L_s} + c_{0,0} + c_{1,0}L_s + c_{2,0}L_s^2 + \cdots\right) + L_z\left(\frac{c_{-2,1}}{L_s^2}\right) \quad \text{(S2)}$$

Limit (2): $L_s \to \infty$ at a fixed L_z. In this case, we consider the system as two coaxial charged cylinders - one with a positive charge of a small radius r_0, and the other with a compensating charge of a larger radius $\frac{L_s}{2}$, as depicted in Fig. S1 (b). Integrating $\frac{1}{2}|\boldsymbol{E}|^2\epsilon_0$ to find the energy, with $\boldsymbol{E} = \frac{qr}{2\pi L_z \epsilon_0}\left(\frac{1}{r_0^2} - \frac{4}{L_s^2}\right)$ $(r < r_0)$ and $\boldsymbol{E} = \frac{q}{2\pi L_z \epsilon_0}\left(\frac{1}{r} - \frac{4r}{L_s^2}\right)$ $(r_0 < r < L_s/2)$, yields a total energy given by:

$$E_{tot} = \frac{q^2}{8\pi\epsilon_0 L_z}\left[2\ln\left(\frac{L_s}{2r_0}\right) - \frac{3}{2} + \frac{8{r_0}^2}{{L_s}^2} + \frac{{r_0}^4}{2}\left(\frac{1}{{r_0}^2} - \frac{4}{{L_s}^2}\right)^2 - \frac{8{r_0}^4}{{L_s}^4}\right]$$
$$= \frac{q^2}{8\pi\varepsilon_0 L_z}\left[2\ln\left(\frac{L_s}{2r_0}\right) - 1 + \frac{4{r_0}^2}{{L_s}^2}\right] \quad \text{(S3)}$$

As the resulting divergence is only logarithmic in L_s, the coefficients for all terms which are either linear or higher order in L_s must vanish. By comparing Eq. (S3) with Eq. (S2), it is clear that

$$c_{ij} = 0 \text{ for } i > 0,$$

and hence Eq. (S2) is further reduced to

$$IE(L_s, L_z) = \cdots + \frac{1}{L_z^2}\left(\cdots + \frac{c_{-2,-2}}{L_s^2} + \frac{c_{-1,-2}}{L_s} + c_{0,-2}\right) + \frac{1}{L_z}\left(\cdots + \frac{c_{-2,-1}}{L_s^2} + \frac{c_{-1,-1}}{L_s} + c_{0,-1}\right)$$
$$+ \left(\cdots + \frac{c_{-2,0}}{L_s^2} + \frac{c_{-1,0}}{L_s} + c_{0,0}\right) + L_z\left(\frac{c_{-2,1}}{L_s^2}\right), \quad \text{(S4)}$$

where the second term

$$\frac{1}{L_z}\left(\cdots + \frac{c_{-2,-1}}{L_s^2} + \frac{c_{-1,-1}}{L_s} + c_{0,-1}\right) = \frac{q^2}{8\pi\varepsilon_0 L_z}\left[2\ln\left(\frac{L_s}{2r_0}\right) - 1 + \frac{4{r_0}^2}{{L_s}^2}\right] + g(L_s)/L_z,$$

with $g(L_s)$ being the remaining absolutely convergent part of the series. In other words,

$$IE(L_s, L_z) = \cdots + \frac{1}{L_z^2}\left(\cdots + \frac{c_{-2,-2}}{L_s^2} + \frac{c_{-1,-2}}{L_s} + c_{0,-2}\right) + \frac{1}{L_z}\left\{\frac{q^2}{8\pi\varepsilon_0}\left[2\ln\left(\frac{L_s}{2r_0}\right) - 1 + \frac{4{r_0}^2}{{L_s}^2}\right] + g(L_s)\right\} + \left(\cdots + \frac{c_{-2,0}}{L_s^2} + \frac{c_{-1,0}}{L_s} + c_{0,0}\right) + L_z\left(\frac{c_{-2,1}}{L_s^2}\right). \quad \text{(S5)}$$

Limit (3): $L_s = L_z = L \to \infty$. It is widely accepted that, in this limit, the calculated ionization energy converges to the actual ionization energy [e.g., PRX 4, 031044 (2014), Ref. 27 in the main text]: $IE(L_s = L_z \to \infty) = IE_0$. By taking the limit using Eq. (S5), we obtain

$$\lim_{L\to\infty} IE(L, L) =$$

$$\lim_{L\to\infty}\left\{\cdots+\frac{1}{L^2}\left(\cdots+\frac{c_{-2,-2}}{L^2}+\frac{c_{-1,-2}}{L}+c_{0,-2}\right)+\frac{1}{L}\left(\frac{q^2}{8\pi\varepsilon_0}\left[2\ln\left(\frac{L}{2r_0}\right)-1+\frac{4{r_0}^2}{L^2}\right]+g(L)\right)+\left(\cdots+\frac{c_{-2,0}}{L^2}+\frac{c_{-1,0}}{L}+c_{0,0}\right)+L\left(\frac{c_{-2,1}}{L^2}\right)\right\}=IE_0. \tag{S6}$$

We see that only a single term in Eq. (S6) survives, which is $c_{0,0}$. Hence, $c_{0,0}=IE_0$.

If we keep in Eq. (S5) all the terms that diverge at least as fast as $1/L_s$ and $1/L_z$, then

$$IE(L_s,L_z)=\frac{1}{L_z}\left[\frac{\mathrm{q}^2}{4\pi\epsilon_0}\ln\left(\frac{L_s}{2r_0}\right)+c_{0,-1}\right]+\left(\frac{c_{-1,0}}{L_s}+IE_0\right)+L_z\left(\frac{c_{-2,1}}{L_s^2}\right), \tag{S7}$$

where, by definition, $c_{0,-1}=$ [the constant term in $g(L_s)$] $-\frac{q^2}{8\pi\varepsilon_0}$.

For 2D systems, ***which is the case presented in the main text***, we maintain $L_z \gg L_s$. Hence, we can ignore the first term in Eq. (S7) to obtain

(2D) $$IE(L_s,L_z)=\left(\frac{c_{-1,0}}{L_s}+IE_0\right)+L_z\left(\frac{c_{-2,1}}{L_s^2}\right)=IE_0+\frac{\alpha}{\sqrt{S}}+\frac{\beta L_z}{S}, \tag{S8}$$

where we have replaced L_s by S, the lateral area of the supercell. Equation (S8) is identical to Eq. (4) in the main text (but obtained by using the result of Ref. [37] and other physical considerations).

For 1D systems, we maintain $L_s \gg L_z$. Hence, we can ignore the $c_{-1,0}$ term and the last term in Eq. (S7) to obtain

(1D) $$IE(L_s,L_z)=\frac{1}{L_z}\left[\frac{\mathrm{q}^2}{4\pi\epsilon_0}\ln\left(\frac{L_s}{2r_0}\right)+c_{0,-1}\right]+IE_0=IE_0+\frac{1}{L_z}\left[\frac{\mathrm{q}^2}{4\pi\epsilon_0}\ln\left(\frac{\sqrt{S}}{2r_0}\right)+\gamma\right]. \tag{S9}$$

The $\frac{1}{L_z}\ln\sqrt{S}$-divergent term in Eq. (S9) is reminiscent of the divergence of a uniformly charged 1D line, as derived in Ref. [S1].

[S1] T.-L. Chan, S. B. Zhang, and J. R. Chelikowsky, Phys. Rev. B **83**, 245440 (2011).

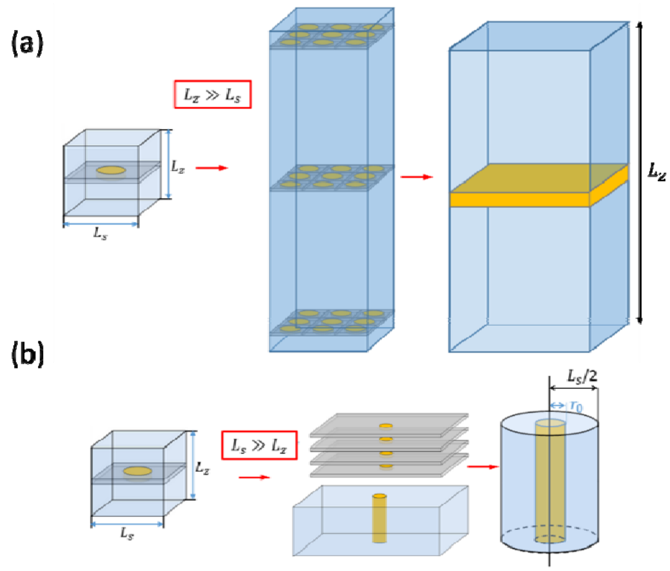

FIGURE S1 (color online). Schematic which illustrates how the electrostatic energy of the localized charged defect (shown in yellow) in a quasi-two dimensional system (shown in gray) with a compensating background (shown in blue) approaches the continuous electrostatic problems of (a) a charged plane in a uniformly compensating background for and (b) a charged cylinder with a uniformly compensating background for . Note that in this case the cylindrical shape of the background, whose density will approach zero, is chosen for mathematical convenience.