**Supplementary Materials for**

**“****Accurate Determination of Formation and Ionization Energies of Charged Defects in Two-Dimensional** **Materials”**

**Analytic expression for the asymptotic behavior of .**

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 ) and . We formally expand the ionization energy in the two variables, and , as follows:

(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) , (2), , and (3) . This greatly simplifies the expansion, which we then approximate for the presented case of .

**Limit (1)**: at a fixed . As depicted in Fig. S1 (a), when 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 , where is the electric field and , to arrive at This linear divergence of the charged system directly leads to a divergent ionization energy with increasing . Explicitly, we can write the ionization energy in this limit as, where is the remaining part of the ionization energy which is non-divergent in . When compared with Eq. (S1), we see that all the coefficients that contain or higher order must vanish from the expansion. In other words, for and for with . This reduces Eq. (S1) to

(S2)

**Limit (2):** at a fixed . In this case, we consider the system as two coaxial charged cylinders - one with a positive charge of a small radius , and the other with a compensating charge of a larger radius , as depicted in Fig. S1 (b). Integrating to find the energy, with and, yields a total energy given by:

(S3)

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

for ,

and hence Eq. (S2) is further reduced to

, (S4)

where the second term

,

with being the remaining absolutely convergent part of the series. In other words,

(S5)

**Limit (3):** . 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]: . By taking the limit using Eq. (S5), we obtain

. (S6)

We see that only a single term in Eq. (S6) survives, which is . Hence, .

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

(S7)

where, by definition, [the constant term in .

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

(2D) , (S8)

where we have replaced by , 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 . Hence, we can ignore the term and the last term in Eq. (S7) to obtain

(1D) (S9)

The -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.