• Charged defects in monolayer (ML) materials using jellium approximation, e.g., BN & MoS$_2$

• Defect-bound ionization of deep levels & carrier transport, e.g., in ML MoS$_2$
  D. Wang, et al., npj Comp. Mater. 5, 8 (2019)

• Charged defects in multi-ML materials, e.g., black P.
  D. Wang, et al., PRB 96, 155424 (2017)
Questions for defects in 2D materials

- Are the defects shallow or deep?
- Can the defects be used in some way for electronic applications?
- How is the physics different from 3D?
- ...

Problem with calculating charged defects in 2D

Consider electron ionization from a point defect

2D:
- Jellium background mostly outside the layer; results are meaningful only when background charge goes to zero.

3D:
- Jellium background inside solid
The electrostatic catastrophe

- As $L_z$ increases, Coulomb energy of a single cell diverges linearly, due to attraction between charged plane and its jellium background charge.
Defect ionization energy \((IE)\) also diverges

\[ \Delta H_f (q = \pm, \alpha) = \Delta H_f (0, \alpha) \pm [\varepsilon_F - \varepsilon(\pm/0)]: \]
\[ \Delta H_f (q = \pm, \alpha) \to \infty \text{ implies } \varepsilon(\pm/0) \to \infty \]

- Defect ionization energy \((IE)\) is defined as

\[ IE(\text{donor}) = \varepsilon_{CBM} - \varepsilon(+/0); \]
\[ IE(\text{acceptor}) = \varepsilon(-/0) - \varepsilon_{VBM}. \]

Hence, they diverge too

- Physically, defect ionization energy cannot diverge, as it determines the electrical behavior of 2D systems.

The physically-correct asymptotic behavior of $IE$

- Consider 2D as a special case of 3D with $L_x = L_y = L_s$

- The true ionization energy $IE_0$ is given by the “dilute limit” provided that $L_z = const \cdot L_s$. Namely, $IE(L_s)\big|_{L_s \to \infty} = IE_0$

- If $L_z \gg L_s$ and $L_z/L_s \neq const$, the problem may be treated as a uniform charged plane in a compensating background, $IE(L_s, L_z) = IE_0 + c_{-2,1} \frac{L_z}{L_s^2}$, where $c_{-2,1} = \frac{q^2}{12\sqrt{3}\epsilon_0}$

- Numerical calculations show an accuracy up to the third decimal point for $c_{-2,1}$

- If the charge is not uniform, however, there will be a correction term, $IE(L_s, L_z) = \frac{c_{-1,0}}{L_s} + IE_0 + c_{-2,1} \frac{L_z}{L_s^2}$. Phys. Rev. E 86, 046702 (2012)
More rigorous solution: expansion of $IE(L_s, L_z)$

$$IE(L_s, L_z) = \sum_{i,j=-\infty}^{\infty} c_{i,j} L_s^i L_z^j$$

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

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

$$+ \left( \cdots + \frac{c_{-2,0}}{L_s^2} + \frac{c_{-1,0}}{L_s} + c_{0,0} + c_{1,0} L_s + c_{2,0} L_s^2 + \cdots \right)$$

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

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

$$+ \cdots$$

**Strategy:** determine non-zero $c_{i,j}$ by taking three physical limits for which $IE(L_s, L_z)$ is known analytically: (1) fix $L_s$, let $L_z \to \infty$; (2) fix $L_z$, let $L_s \to \infty$; and (3) let $L_s = L_z \to \infty$
Obtaining $IE_0$ using asymptotic expression

- Calculate $IE(L_S, L_z)$ using large enough $L_S$ and $L_z$

- Define $\bar{IE} = IE(L_S, L_z) - \frac{c_{-1,0}}{L_S} = IE_0 + c_{-2,1} \frac{L_z}{L_S^2}$ and fit the results for different $L_S$

- Intercept of the lines with different $L_S$’s yields $IE_0$.

Application to ML BN

- Standard results depend on the supercell size
- Using $\overline{IE} = IE_0 + c_{-2,1} \frac{L_z}{L_s^2}$, easily get $IE_0$ from $\overline{IE}$ intercept with $y$ axis

- Defect levels are exceptionally deep, but consistent with Komsa*.

* PRL110, 095505, (2013); PRX4, 031044 (2014)
Alternate way to view IE in ML BN: the $C_B$ case

- 12 points from first-principles calculations
- Fit to $IE(L_S, L_Z) = \frac{c_{-1,0}}{L_S} + IE_0 + c_{-2,1} \frac{L_Z}{L_S^2}$ with only two parameters $IE_0$ and $C_{-1,0}$

- $IE_0$ here is within 100 meV of brute-force extrapolation using cubic supercells up to 19x19x19 (inset).

Monolayer MoS$_2$

- Similar to BN, good linear fits are also obtained.

Wang, et al., npj Comp. Mater. 5, 8 (2019)
Among native defects, $V_S$ is most easy to form

Extrinsic dopants Nb and Re also have low formation energies

DOS show shallow donor/acceptor levels for Re/Nb, which are, however, at variance with calculated defect transition energies.

* red lines are impurity DOS x 10
What do we know from experiments?

- Measured carrier mobilities are noticeably smaller than theoretical band edge mobilities, which calls for a new theory to explain.

Table 1: Elemental substitutional doping of several typical MXs and their electrical doping behaviour

<table>
<thead>
<tr>
<th>MX_n</th>
<th>Dopant</th>
<th>Type</th>
<th>Concentration [cm⁻²]</th>
<th>Mobility [cm² V⁻¹ s⁻¹]</th>
<th>Band-edge mobility [theory]</th>
</tr>
</thead>
<tbody>
<tr>
<td>MoS₂</td>
<td>Nb</td>
<td>p</td>
<td>1.8 × 10¹⁴</td>
<td>14</td>
<td>130¹, 420², 225³, 340⁴</td>
</tr>
<tr>
<td></td>
<td>P</td>
<td>p</td>
<td>10⁻¹⁰–10¹²</td>
<td>137.7</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Re</td>
<td>n</td>
<td>5.5 × 10¹²</td>
<td>—</td>
<td></td>
</tr>
<tr>
<td>MoSe₂</td>
<td>W</td>
<td>p</td>
<td>4.0 × 10¹¹</td>
<td>1.6</td>
<td>240⁴,</td>
</tr>
<tr>
<td></td>
<td>N</td>
<td>p</td>
<td>3.83 × 10¹¹</td>
<td>1.7</td>
<td>1100⁴,</td>
</tr>
<tr>
<td></td>
<td>Cl</td>
<td>n</td>
<td>6.0 × 10¹¹</td>
<td>60</td>
<td></td>
</tr>
<tr>
<td>WSe₂</td>
<td>S</td>
<td>n</td>
<td>—</td>
<td>68.2</td>
<td>705⁴,</td>
</tr>
<tr>
<td>Cl₂</td>
<td>Fe</td>
<td>n</td>
<td>—</td>
<td>42</td>
<td></td>
</tr>
</tbody>
</table>

https://pubs.rsc.org/en/content/articlelanding/2019/nh/c8nh00150b#!divAbstract
Defect-bound ionization: $IE_1$ versus $IE_{\infty}$

- When a donor is fully ionized ($IE_{\infty} = IE_0$), its electron is fully delocalized. In the extreme case, the electron becomes a plane wave $\rightarrow$ jellium model.
- When the donor is not fully ionized, the electron is bounded. To calculate the lowest-energy defect-bound state ($IE_1$), we use the constraint DFT, which is identical to the approach recently proposed by Pantelides et al.

Note: hydrogenic model is not expected to work; used here only for illustration purpose.
$E_{db}$ in defect transition energy scheme

Wang, et al., npj Comp. Mater. 5, 8 (2019)

- Similar to hBN, full ionization of any of the defect is difficult.
- $IE_1$ is noticeably smaller than $IE_\infty$, which can be attributed to the sizable $E_{db}$, which can also be viewed as exciton binding energy at the defect.
Localization of defect states

Wang, et al., npj Comp. Mater. 5, 8 (2019)

- Small cell = 7x7 147-atom cell; large cell = 13x13 507-atom cell
- Density contour normalized to hole density: large cell = 0.3 × small cell
- A larger $E_{db}$ correlates with a higher degree of hole localization.
Re donor band & wavefunction overlap

- Re density is at 5x10^{12} \text{ cm}^{-2}
- Noticeable dispersion of donor band with larger $\mu$
- Noticeable overlap between defect wavefunctions → transport within defect band

- For real defects, one needs evaluate the critical defect density at percolation threshold. Wang, et al., npj Comp. Mater. 5, 8 (2019)
More general situation when $d_0$ is finite & $L_x \neq L_y$

Wang, et al., PRB 96, 155424 (2017)

- Yellow star = defect

(a) – the $L_z \gg L_x (L_y)$ limit

(b) – the $L_x (L_y) \gg L_z$ limit.
For $L_y = L_x = L_s$, we had

$$IE(L_s, L_z) = \frac{c_{-1,0}}{L_s} + IE_0 + c_{-2,1} \frac{L_z}{L_s^2}$$

For $L_y = \gamma L_x$, we have, instead

$$IE(L_x, L_z) = \frac{c_{-2,0}}{L_x^2} + \frac{c_{-1,0}}{L_x} + IE_0 + c_{-2,1} \frac{L_z}{L_x^2}$$

$$= IE_0 + \frac{c_{-1,0}}{L_x} + c_{-2,1} \frac{L'_z}{L_x^2}$$

where $L'_z = (L_z - 4d_0) - 2d_0(1 - \varepsilon_\perp^{-1})$ with $\varepsilon_\perp = \text{out-of-plane relative dielectric constant}$.

Wang, et al., PRB 96, 155424 (2017)
Defects in ML-BP: $V_P$, $P_i$, & $X_P$ ($X = O, S, Se,$ and Te)

- All defects are deep with donor levels near VBM, instead of CBM.

- At $V_P^0$, 3 second-neighbor P atoms form (trimer) bonds.

- Substitutional impurities have noticeably small formation energies (negative for $O_P$).

$E_{g}^{PBE} : 0.91$ eV
Dependence on the layer thickness: $T_e$ in BPs

- Critical difference can already be seen at bilayer, which represents a 36% reduction in $IE_0$.
- Technical: $L_z^T$ stands for $L_z$ for which $L_z^{-1}$ and $L_z^{-2}$ terms in the expansion can be ignored.
- $IE_0$ monotonically decreases with layer thickness.

Wang, et al., PRB 96, 155424 (2017)
Charge localization & depth of defect level: $\text{Te}_P$

- Charge localization in the $z$-direction strongly correlates with the depth of the defect levels.
- ... but to a lesser degree in either $x$- or $y$-direction.
Challenges & opportunities

- **Challenges**: 2D appears to have universally very-deep defect transition energies

- **Opportunities**: utilizing the defect-bound 1st excited state or few-layer 2D structures for carrier transport

- *The true difference between 2D and 3D is in the reduced dielectric screening.*