Band alignment

... relevance to bulk properties
Deformation potential

\[ a_i = \frac{\Delta E_i}{\Delta \ln V} \]

where \( \Delta E_i \) is the shift in energy level under strain and \( \Delta \ln V \) is the change in volume.

- Since **there is no common reference when volume changes**, energy levels between strained and unstrained systems cannot be compared.

- Model solid theory
  - Van de Walle-Martin (1989)

- Core level alignment
  - Wei-Zunger (1999)

- Lattice harmonic expansion
  - Li-Gong-Wei (2006)
Formation energy of a charged defect

\[ \Delta H_f(q, E_F) = \Delta E + q(E_{VBM} + E_F) \]

Two issues of fundamental concerns:

1. Interaction of a charged defect with its periodic images
   - Makov-Payne correction (1995)
   - Lany-Zunger scheme (2008)
   - Freysoldt et al. scheme (2009)

2. No common reference of \( E_{VBM} + E_F \) for charged/neutral systems
   - Typically, compare electrostatic potentials far away from defect.
Band alignment

... relevance to interfacial properties
Band alignment in electronic devices

Metal/semiconductor junction:

\[ E - E_F = q\phi_B \]

p-n junction:

\[
\begin{array}{c|c}
\text{N type} & \text{P type} \\
N_d & N_a \\
\end{array}
\]

Hetero junction:

Type I: Straddling alignment

Type II: Staggered lineup
Band alignment in photo-electrochemical cell

... for water splitting:

Nat. Rev. Mater. 1, 15010 (2016)
Band alignment in a Galvanic circuit

Schematic potential profile:

Galvani (inner) potential

Potential across cell = $eV_{oc}$
However, reference for the alignment is missing

... because the material’s intrinsic quantity – the average electrostatic potential of the bulk $\bar{V}$ – is “ill-defined”:

- $\bar{V} = \frac{1}{\Omega} \int_{\text{unit cell}} \int_{\infty}^{\rho(r)} dr \, dr'$ is conditionally convergent, depending on how the integral is taken.

- In a Fourier space representation, $\bar{V} = \lim_{G \to 0} V(G)$ depends on the direction from which the limit is taken.

Kleinman, PRB 24, 7412 (1981)
It is perceived that average potential $\bar{V}$ has no physical meaning. In DFT calculations, however, we always set $\bar{V} = 0$, which eliminates its orientation dependence.

Rather, the vacuum level becomes orientation dependent, if a surface is introduced!
This places us at disadvantages
Molecular orbital theory – foundation of quantum chemistry

\[ H = \begin{bmatrix} \varepsilon_{1s} & \Delta_{sp} \\ \Delta_{sp} & \varepsilon_{2p} \end{bmatrix} \rightarrow \varepsilon_{\sigma} \approx \varepsilon_{2p} \frac{\Delta_{sp}^2}{\varepsilon_{1s} - \varepsilon_{2p}}; \varepsilon_{\sigma^*} \approx \varepsilon_{1s} + \frac{\Delta_{sp}^2}{\varepsilon_{1s} - \varepsilon_{2p}} \]

Solid State

- In the absence of a common vacuum level, how to quantify interfacial physics and chemistry?
Consider, for example, built-in potential ($\psi$)

**Definition**: potential difference due to interfacial electric dipole as a result of charge accumulation at interface.
What is the electric dipole, though?

For finite systems, dipole is unambiguously defined.
Ambiguity arises for bulk solids

In a bulk: **Infinite ways to construct a unit cell → infinite number of dipole moments?**

→ solved by analyzing charge response & Berry phase of wavefunctions

*Resta (1992); King-Smith & Vanderbilt (1993)*

At an interface: **no clear way to determine the electric dipole as bulk contribution is ill-defined, so built-in potential is also ill-defined**

→ unsolved problem.
Two schools of thoughts on built-in potential

- **1st school: Constructionist view**
  - $\psi$ is determined by properties of individual materials
  - What property describes the built-in potential?
    - Work function, electronegativity, Galvani potential, etc.
  - It led to many notorious failures in interfacial science (e.g., Schottky-Mott rule)

- **2nd school: Non-constructionist view**
  - $\psi$ is specific to a particular interface
  - How to define the built-in potential?
    - Ill-defined interfacial dipole methods are often used.
Redefine built-in potential using potential, NOT charge

- Let us introduce a new quantity $V^0$, which is an intrinsic property of a bulk crystal
- As $V^0$ is with respect to the average potential $\bar{V}$, it’s value will depend on the direction of the crystal
- At an A/B interface, the built-in potential is given by

\[
\psi_{A|B} \equiv V_B^0 - V_A^0.
\]

Choe, West, & S. Zhang, PRL 121, 196802 (2018)
Construction of an ideal interface

\[ V_{A}^{iv} = V_{A}^{0} = \text{maximum } V \]

 Ideal interface

\[ V_{A}^{iv} + V_{B}^{iv} = V_{A}^{0} + V_{B}^{0} \]
\[ = \text{new } V_{A}^{0} \]
\[ = \text{new } V_{B}^{0} \]

new \( V_{A}^{0} \) = new \( V_{B}^{0} \) maximum values again align

Relaxed interface

\[ \psi_{A|B} = V_{B}^{0} - V_{A}^{0} \]

Interface dipole

Choe, West, & S. Zhang, PRL 121, 196802 (2018)
V$^0$ is UNIQUE

A. Boundary $z'$ at $V = V^0$

B. Ideal vacuum insertion

Boundary $z'$ is chosen such that dipole is zero

$$\int_{z'}^{z'+a} \rho(z) zdz = 0$$

After integration by parts,

$$zE(z)|_{z'}^{z'+a} - \int_{z'}^{z'+a} E(z)dz = aE(z') = 0$$

Hence,

$$E(z') = -\nabla V(z') = 0$$

From the above, $z'$ is where the electric field is zero, so the insertion of vacuum has no effect on the potential inside the bulk region → both $z'$ and $V^0$ are unique.
$V^0$ is UNIQUE (continue)

A. Boundary at $V = V^0$

B. Ideal vacuum insertion

C. Boundary at $V \neq V^0$

D. Non-ideal vacuum insertion

With a non-vanishing dipole, both $V$ (bulk) & vacuum level are ill-defined.

Choe, West, & S. Zhang, PRL 121, 196802 (2018)
A different perspective

- The planar average leaves us with a 1D system made of infinitely-large charge plates perpendicular to $z$. In the absence of monopole and dipole, potentials outside the unit cell are fixed at $V = 0$.

As such, the potential must satisfy:
Interfacial dipole no longer ambiguous

- Once the bulk cell is uniquely defined, the interfacial region is also uniquely defined

- ... so do its charge density and interfacial dipole

- The potential approach and the charge density approach are NOW completely equivalent and complement each other.

Choe, West, & S. Zhang, PRL 121, 196802 (2018)
Direct evidence of $V^0$ alignment from DFT

Choe, West, & S. Zhang, PRL 121, 196802 (2018)
Direct evidence of $V^0$ alignment from DFT

Si/Ge

Ca$_2$N/MoTe$_2$

AFTER electronic relaxation

Choe, West, & S. Zhang, PRL 121, 196802 (2018)
NO electronic relaxation is a key in order to make a connection of an interface with its intrinsic bulk properties.

The only way to trace bulk genes!
### Ideal band offsets meet reality

- **Schottky barriers in van der Waals heterojunctions (NOT 2D)**

<table>
<thead>
<tr>
<th>orientation</th>
<th>V\textsuperscript{iv} align (eV)</th>
<th>Reference (eV)</th>
<th>Absolute diff.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1T’-MoTe\textsubscript{2}/2H-MoTe\textsubscript{2}</td>
<td>c-axis 1.12</td>
<td>1.24</td>
<td>0.12</td>
</tr>
<tr>
<td>2H-NbSe\textsubscript{2}/2H-WSe\textsubscript{2}</td>
<td>c-axis 0.83</td>
<td>0.80</td>
<td>0.03</td>
</tr>
</tbody>
</table>

*Science 349, 625 (2015); JJAP. 56, 04CK09 (2017); ACS Nano 11, 3904 (2017)*

- **Valence band offsets in traditional semiconductor junctions (MAD~0.17 eV)**

<table>
<thead>
<tr>
<th>orientation</th>
<th>V\textsuperscript{iv} align (eV)</th>
<th>Reference (eV)</th>
<th>Absolute diff.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si/AlP (110)</td>
<td>1.12</td>
<td>1.24 (theory)</td>
<td>0.12</td>
</tr>
<tr>
<td>Si/GaP (110)</td>
<td>0.83</td>
<td>0.80</td>
<td>0.03</td>
</tr>
<tr>
<td>AlP/GaP (100)</td>
<td>-0.23</td>
<td>-0.50</td>
<td>0.27</td>
</tr>
<tr>
<td>Ge/GaAs (110)</td>
<td>0.76</td>
<td>0.52</td>
<td>0.24</td>
</tr>
<tr>
<td>Ge/AlAs (110)</td>
<td>1.04</td>
<td>0.93</td>
<td>0.11</td>
</tr>
<tr>
<td>GaAs/AlAs (100)</td>
<td>0.21</td>
<td>0.50</td>
<td>0.29</td>
</tr>
<tr>
<td>GaAs/AlAs (110)</td>
<td>0.28</td>
<td>0.40</td>
<td>0.12</td>
</tr>
</tbody>
</table>
Two general features of the theory

- Neither a complex boundary condition at interface, nor a shrinkage/expansion of the bulk materials, can cause ambiguities in the new definition.

- The definition is universal and for all types of interfaces:
  - For example, grain boundary, polar/non-polar, order/disorder, solid/amorphous (or liquid), ... or even gas/gas interfaces.
  - Surfaces = solid/vacuum interfaces.
An alternative to ideal vacuum insertion: *the no vacuum approach*

Choe, West, & S. Zhang (arXiv:1906.10162)
Electrostatic potential

For a finite system where $\rho(r) =$ total charge (electrons + ions),

$$V(r) = \int \frac{\rho(r')}{|r - r'|} \, dr',$$

satisfying $V(|r| \to \infty) = 0$

For an infinite system, $V_\infty(r) = \int_\infty \frac{\rho(r')}{|r - r'|} \, dr'$

Here, however, we can no longer determine where is

$$V(|r| \to \infty) = 0$$

Note: it is not that the reference vacuum level is ill-defined, but we lose track of it.
Consider the average potential

For the infinite system, average potential is defined as

\[
\bar{V} = \frac{1}{\Omega} \int_{\text{unit cell}} V_\infty(r) \, dr = \frac{1}{\Omega} \int_{\text{unit cell}} \int_\infty \frac{\rho(r')}{|r - r'|} \, dr' \, dr
\]

where each unit cell \((-\infty < n < +\infty \text{ and } n \neq 0\)) contributes to potential \(V_\infty(r)\) in central \(n = 0\) cell.

In other words, \(V_\infty(r)\) decomposes into contributions from individual cells.
Unfolding the potential of (central) cell 0

Real-space potential

Brillouin zone analogue

Energy dispersion of a free electron
Reformulating the integration

By the unfolding scheme:

\[ \int_{\text{unit cell}} V_\infty(\mathbf{r}) d\mathbf{r} = \int_\infty V_{\text{unit cell}}(\mathbf{r}) d\mathbf{r} \]

where \( V_{\text{unit cell}}(\mathbf{r}) = \int_{\text{unit cell}} \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' \).

Basically, contribution of the \( n \)th cell at the 0th cell equals that of the 0th cell at the \( n \)th cell.
Recover vacuum level position for \( \bar{V} \)

Hence,

\[
\bar{V} = \frac{1}{\Omega} \int_{\infty} \Delta V_{\text{unit cell}}(\mathbf{r}) d\mathbf{r}
\]

Notice that vacuum level position is given NOW by \(|\mathbf{r}| \to \infty, V_{\text{unit cell}}(|\mathbf{r}| \to \infty) = 0\), so \( \bar{V} \) is actually calculated with respect to the true vacuum level.

Recover the reference vacuum level position we had LOST earlier!

Choe, West, & S. Zhang (arXiv:1906.10162)
Relation between $V^0$ and $\bar{V}(\hat{n})$

- Let $V^0$ be the orientation-independent vacuum level and $\bar{V}(\hat{n})$ be an orientation-dependent average potential.

- Then, $\bar{V}(\hat{n}) = V^0 + \int_{\infty} \text{V}_{\text{unit cell}}(r)dr$

- The integration ($\int_{\infty} \text{V}_{\text{unit cell}}(r)dr$) is a quadrupole that accounts for all the orientation dependence of $\bar{V}(\hat{n})$. 
Comparison with vacuum insertion

- $\tilde{V} - V^0$ here are in perfect agreement with those from vacuum insertion → the two approaches are completely equivalent.

- Nevertheless, the physical meaning of $\tilde{V}$ becomes clear for the first time: intrinsic quadrupole shift from $V^0$. 

Choe, West, & S. Zhang (arXiv:1906.10162)
A remaining issue as reflected in these model studies

- With respect to $V^0 (= 0)$, $\bar{V}(\hat{n})$ can be strongly orientation-dependent.

- One can remove such a dependence but only if one does not cut through the “atoms”.

- Not possible but if chemists were correct, we should never cut through atoms. HOW?

Choe, West, & S. Zhang (arXiv:1906.10162)
Aside ...

- The issue of cutting into atoms also suggests that calculating $V(\mathbf{r})$ (and $\bar{V}$) should use exact potential and actual charge density, i.e., core electron density + valence electron density + point ionic charges.
- ... rather than a soft pseudopotential and its pseudo charge density.
- This can be done either by a core correction or an all-electron approach.

Choe, West, & S. Zhang (arXiv:1906.10162)
Summary

- The longstanding problem of vacuum-level position in a periodic bulk solid is solved.
- Our findings, in a simple way, unify ALL themes of band alignments in matter.
  - It sheds lights on the physics of deformation potential, Schottky barrier height, band offsets.
  - It also sheds lights on electrochemistry such as Galvani, electrode, and redox potentials.