

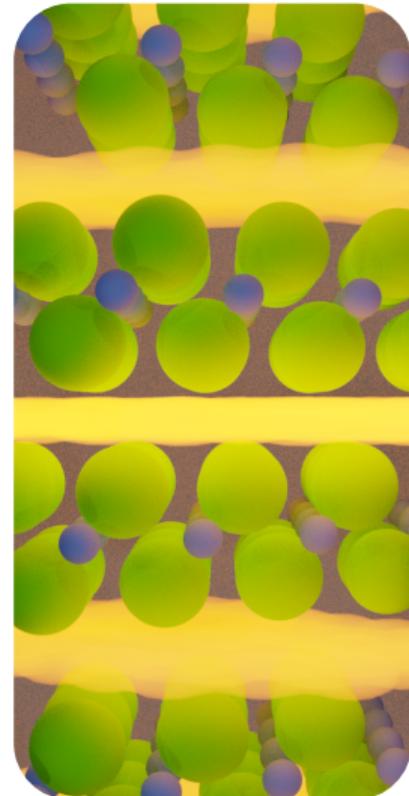
LAYERED ELECTRIDES

What They Are, What They Do, and What Can They Do

Adrian F. Rumson

Department of Chemistry
Dalhousie University

University of Cambridge
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Acknowledgements



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Introduction

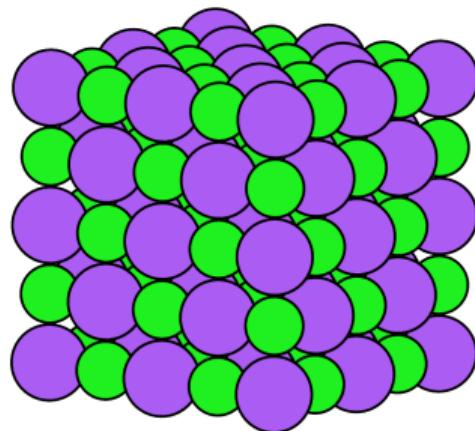
Thermal Expansion

2D Semiconductors

Conclusions

Motivation: Ionic Materials

Consider NaCl:

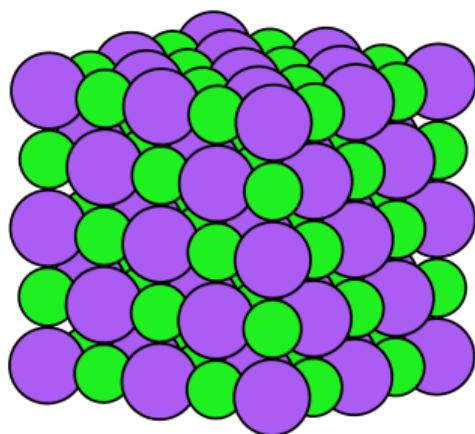


Simple cubic lattice ($Fm\bar{3}m$) composed of sodium cations and chloride anions:



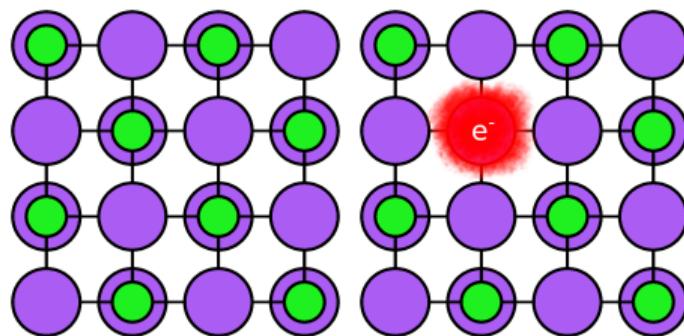
Motivation: Ionic Materials

Consider NaCl:



Simple cubic lattice ($Fm\bar{3}m$) composed of sodium cations and chloride anions:
 $[Na^+][Cl^-]$

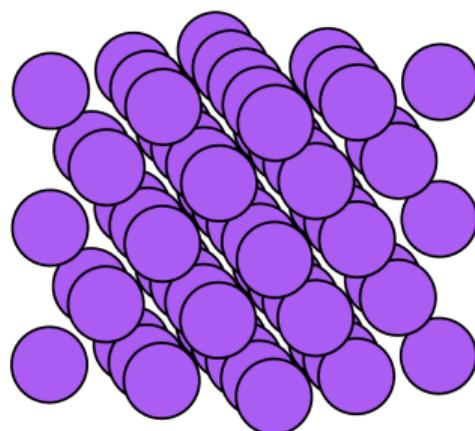
F-centers (*Farbzentrum*):



A crystallographic defect where an anion's position is vacant, but its electron(s) remain.

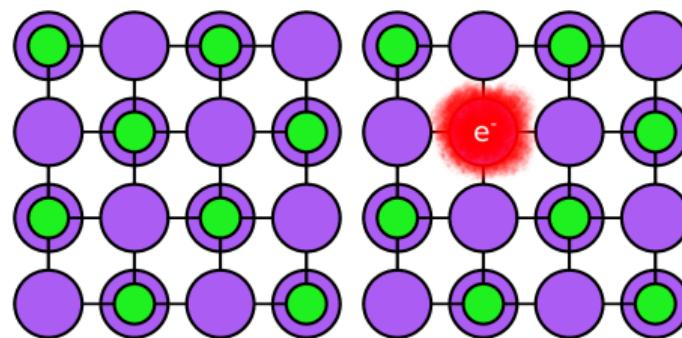
Motivation: Ionic Materials

What if every anion was an F-center?



That would leave you with an ionic crystal of sodium $[\text{Na}^+]:\text{e}^-$.

F-centers (*Farbzentrum*):

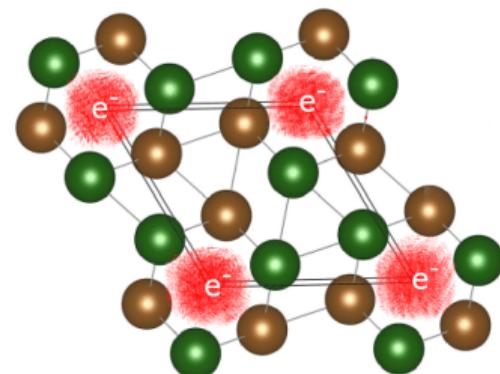


A crystallographic defect where an anion's position is vacant, but its electron(s) remain.

Electride

DEFINITION: An ionic material where a localized electron acts in the place of an anion.

Sodium metal, under extreme conditions (250–350 GPa, 710–1900 K), becomes an electride.



Other materials can exhibit electride character under ambient conditions.

- $[\text{Ca}_{24}\text{Al}_{28}\text{O}_{64}]^{4+} : 4\text{e}^-$
 - $[\text{AE}_2\text{Pn}]^+ : \text{e}^-$, $[\text{M}_2\text{C}]^{2+} : 2\text{e}^-$

Electrides are often notated as neutral,
e.g. Ba_2N .

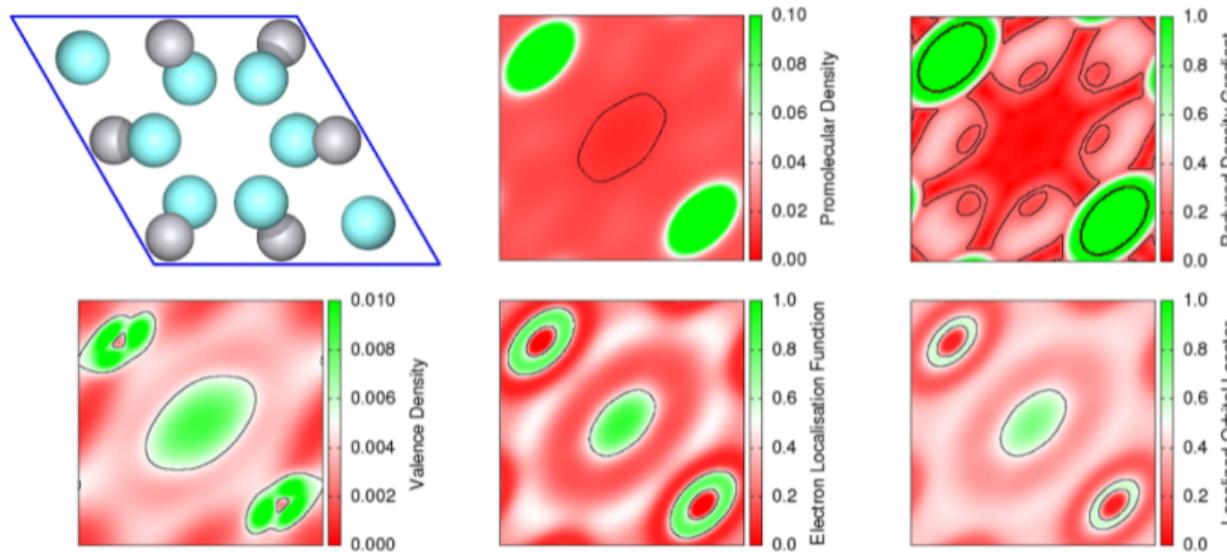
Electride character is often only recognized years or decades post initial synthesis.

How are electrides identified?

Some electrides can be identified with NMR or other experimental methods.



Most electrides are identified with computational visualization methods. (*viz.* Y_5Si_3)



ELF and ILDOS

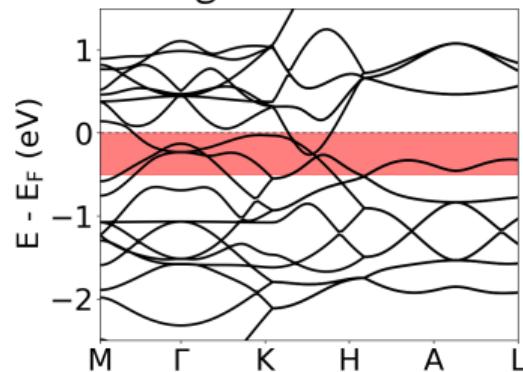
Two popular methods for visualization for identifying of electrides are the *electron localization function* (ELF):

$$D_\sigma(\mathbf{r}) = \tau_\sigma(\mathbf{r}) - \frac{1}{4} \frac{(\nabla \rho_\sigma(\mathbf{r}))^2}{\rho_\sigma(\mathbf{r})}$$

$$D_\sigma^{\text{UEG}}(\mathbf{r}) = c \rho_\sigma^{5/3}(\mathbf{r})$$

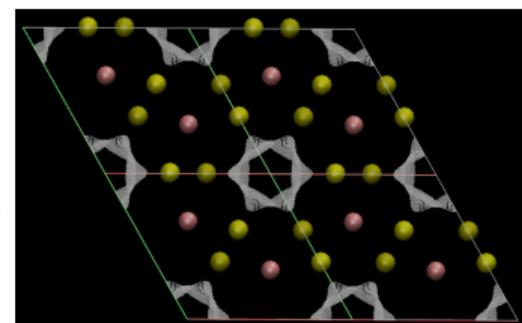
$$\text{ELF}(\mathbf{r}) = \frac{1}{1 + \left(\frac{D_\sigma(\mathbf{r})}{D_\sigma^{\text{UEG}}(\mathbf{r})} \right)^2}$$

and the *Integrated Local Density of States* (ILDOS):



Projection to \mathbb{R}

Integration

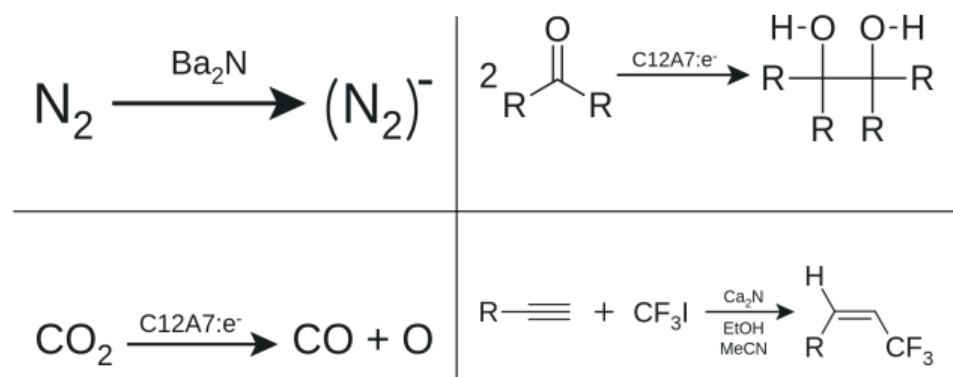


What can they do?

Electrides are powerful reducing agents/have a very low work function.

Chemical Applications:

- Nitrogen splitting (E_A of 35 kJ/mol *comparari* 108 kJ/mol with Ru/MgO)¹
 - CO₂ splitting²
 - Pinacol coupling³
 - Hydrotrifluoromethylation of alkenes and alkynes⁴



[1] Zhang et al., *J Am. Chem. Soc.*, 2023, 145, 24482

[2] Toda et al., *Nat. Commun.*, 2013, 4, 2378.

[3] Buchammaga *et al.*, *Org. Lett.*, **2007**, *9*, 2007.

[4] Choi, et al., *Nat. Commun.*, 2014, 62, 12137.

What can they do?

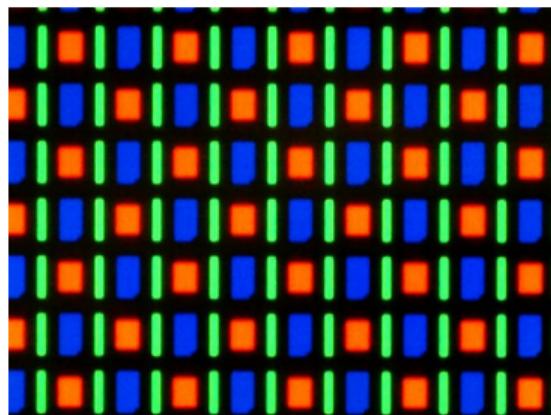
Electrides are powerful reducing agents/have a very low work function.

Electronics Applications:

- Sodium ion battery anodes¹
- Electron injection layers in OLEDs²

Other Physical Properties

- Superconductivity (not high-T)³
- Magnetism⁴



Microscope view of an OLED Display

[1] Hu et al., *ACS Appl. Mater. Interfaces*, **2015**, 7, 24016.

[2] Kim et al., *J. Phys. Chem. C*, **2007**, 111, 8403.

[3] Miyakawa et al., *J. Am. Chem. Soc.*, **2007**, 129, 7270.

[4] Lee et al., *Nat. Commun.*, **2020**, 11, 1526.

Photo courtesy of Matthew Rollings via the Wikimedia Commons.

A Perfect Coalescence

Electrides are a perfect coalescence from the perspectives of theory and application.

- As materials, they are not found in nature, and are thus novel.
- Their ability to act as strong reducing agents can be applied to a variety of applications.
- Their remarkable electronic structure makes them interesting from the theory side.

Classifying Electrides

There are a few schemes to group electrides with similar character:

Organic/Inorganic

Organic electrides are usually salts containing alkali metals.

Many inorganic electrides have been synthesized.

Dimensionality

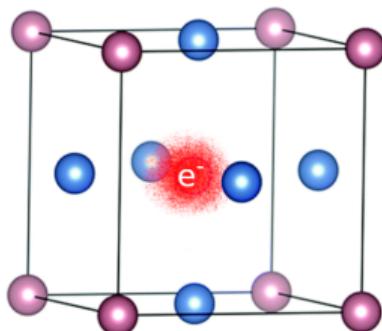
0D, 1D, 2D, 3D

Stoichiometry

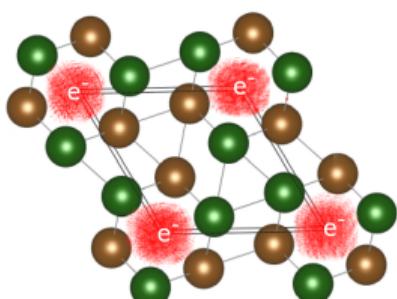
AE_2Pn , M_2C , $AM(\text{cryptand}-i.j.k)_2$, etc.

Dimensionality

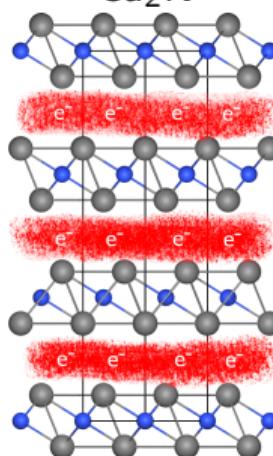
0D Electride:
 Ca_3Pb



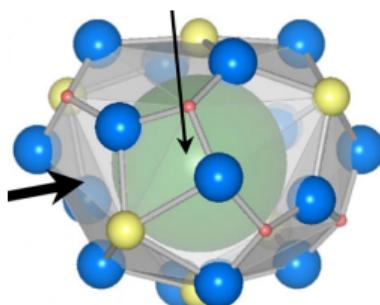
1D Electride:
 $P6_3/m$ Sodium



2D Electride:
 Ca_2N



3D Electride:
 $\text{Ca}_{24}\text{Al}_{28}\text{O}_{64}$



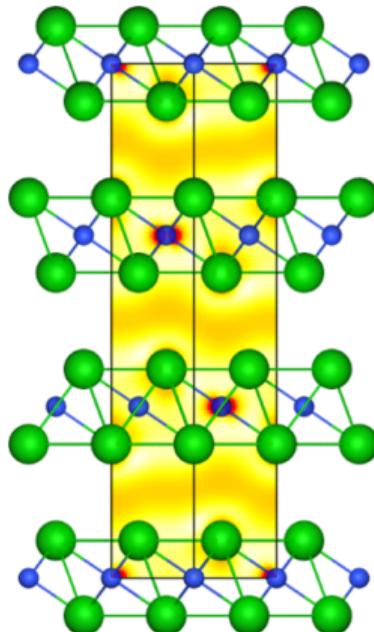
Zhang et al. *J. Mat. Chem. C* 2018 6(3), 575
Wang et al. *Phys. Rev. B*, 2023, 107(18), 184101
Toda et al. *Nature* 2013 4(1), 2379

Layered Electrides

2D Electrides are layered materials where the anionic electron is localized between positively charged sheets.

They can be exfoliated to their monolayers, featuring high surface charge.

These are sometimes called “electrenes.”



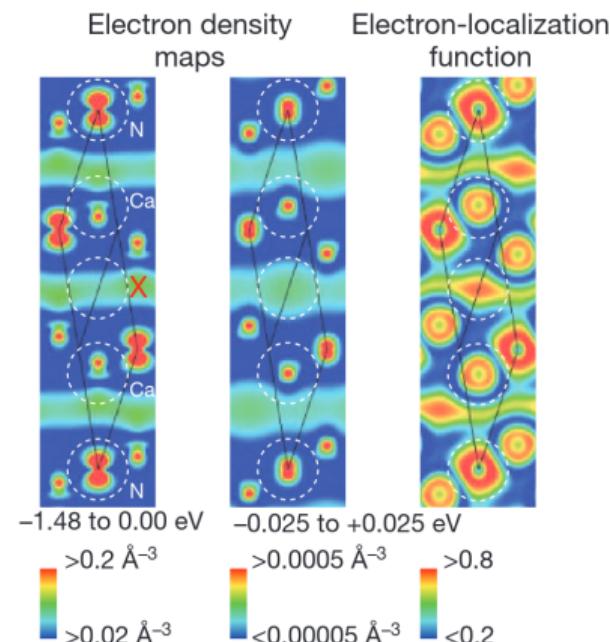
ILDOS plot of Ba_2N , showing 0.5 eV under the Fermi level.

Dicalcium Nitride

Ca_2N was first synthesized in 2002 by reacting Ca_3N_2 with Ca metal at high temperature.

Recognized as an electride in 2013 and exfoliated to a monolayer in 2016.

The electride character of Ca_2N was robustly confirmed by a combination of experiment and DFT.



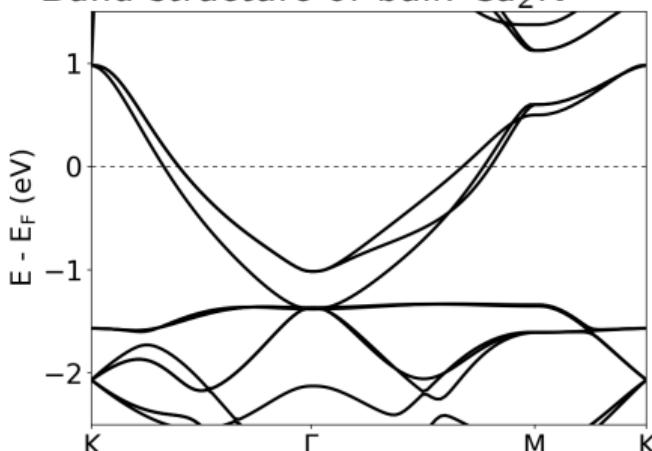
Reckeweg et al., *J. Solid State Sci.*, 2002, 4(5), 575.

Lee et al., *Nature*, 2013, 494, 336.

Druffel et al., *J. Am. Chem. Soc.*, 2016, 138(49), 16089

Dicalcium Nitride

Band structure of bulk Ca_2N



Notable features:

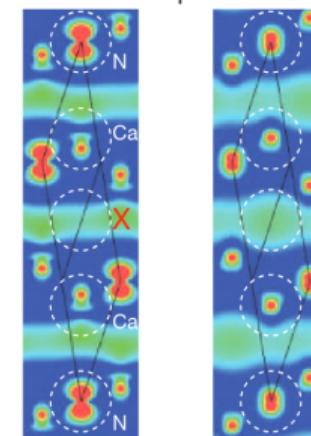
- Metallic
- Minimal DOS around E_F

Reckeweg et al., *J. Solid State Sci.*, 2002, 4(5), 575.

Lee et al., *Nature*, 2013, 494, 336.

Druffel et al., *J. Am. Chem. Soc.*, 2016, 138(49), 16089

Electron density maps



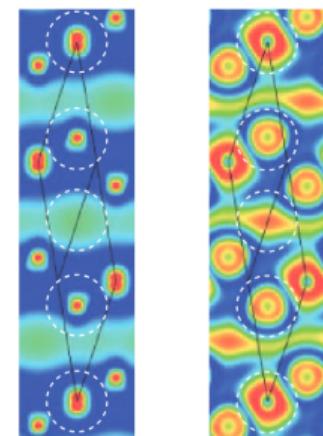
-1.48 to 0.00 eV

>0.2 Å⁻³

>0.02 Å⁻³

>0.00005 Å⁻³

Electron-localization function



-0.025 to +0.025 eV

>0.0005 Å⁻³

>0.8

<0.00005 Å⁻³

The AE₂Pn Electride Class

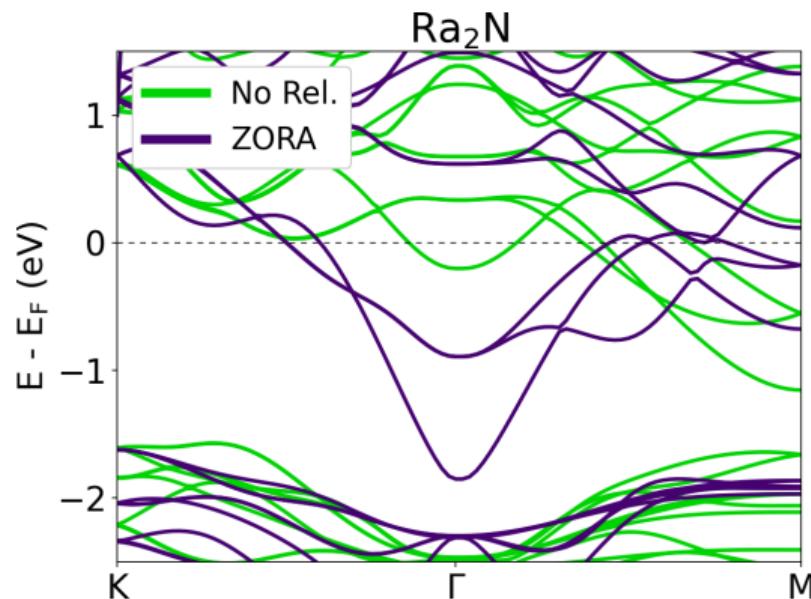
Seven AE₂Pn electrides in the $\bar{R}\bar{3}m$ space group have been theorized:

		AE			
		Ca	Sr	Ba	Ra
Pn	N	Ca ₂ N	Sr ₂ N	Ba ₂ N	Ra ₂ N?
	P	Ca₂P	Sr ₂ P	Ba ₂ P	???
	As	Ca₂As	Sr₂As	Ba ₂ As	???
	Sb	Ca₂Sb	Sr₂Sb	Ba ₂ Sb	???

Of these, only the nitrides (Ca₂N, Sr₂N, Ba₂N) are known experimentally.

A fun thing about Ra_2N

Relativity governs the occupation of the electride state.



Other M₂E Electrides

Transition-metal Carbides ($R\bar{3}m$):

- Y₂C
- Sc₂C

Transition-metal Chalcogenides:

- Ti₂S ($Pnnm$)
- Zr₂S ($Pnnm$)
- Hf₂S_{1-x}Se_x ($P6_3/mmc$)

Lanthanide Carbides ($R\bar{3}m$):

- Gd₂C
- Tb₂C
- Dy₂C
- Ho₂C

Sc₂C and Al₂C (theoretical) are semiconducting electrides, where hybridization of the metal and electride states leads to the opening of a band gap.

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Conclusions

The initial idea

I wanted to know if GGA+D is good enough to model electrides. We narrowed that down to:

How do the following factors influence the accuracy of DFT on layered electrides compared to experiment?

- Type of basis set (PAW versus NAO)
- Functional/Dispersion correction
- Thermal expansion

Compare to layered electrides that have been experimentally characterized with XRD at room temperature: Ca_2N , Sr_2N , Ba_2N , Sc_2C , Y_2C .

Post-SCF Dispersion Corrections

Tkatchenko-Scheffler (TS)

- C_6 dispersion coefficient
- Polarizabilities, homoatomic C_6 coefficients, and van der Waals radii are volume scaled

Grimme's Dispersion Corrections (D3/D3BJ)

- C_6 by Casimir-Polder integral
- C_8 derived from C_6 by recurrence
- Coordination of atoms is considered

Many-Body Dispersion, Non-local (MBD-NL)

- Polarizability by Vydrov and Van Voorhis model
- C_6 by Casimir-Polder integral
- Energy from CFDM Hamiltonian

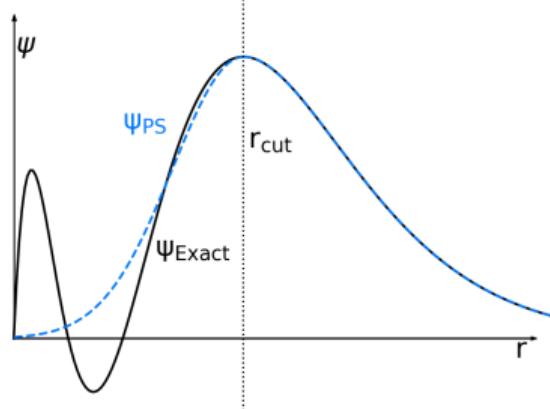
Exchange-Hole Dipole Moment (XDM)

- C_6 , C_8 , C_{10} from multipole moments of Hirshfeld-partitioned electron density
- Polarizabilities are volume scaled

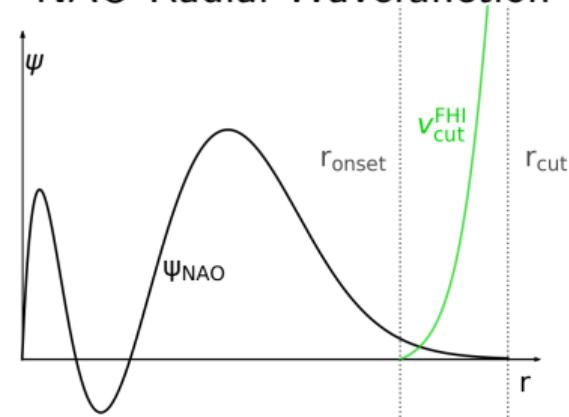
All these dispersion corrections will be paired with PBE, plus B86bPBE-XDM.

Agreement of Basis Sets: PAW versus NAO

PAW Radial Wavefunction

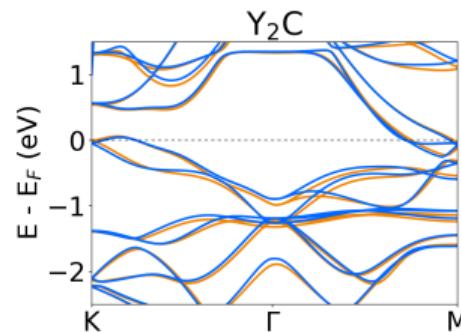
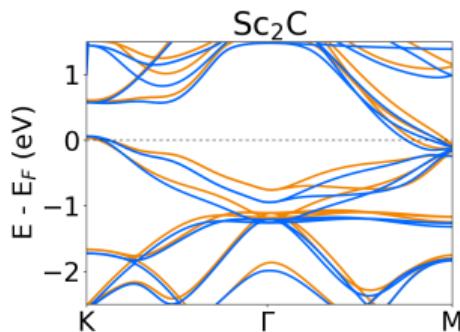
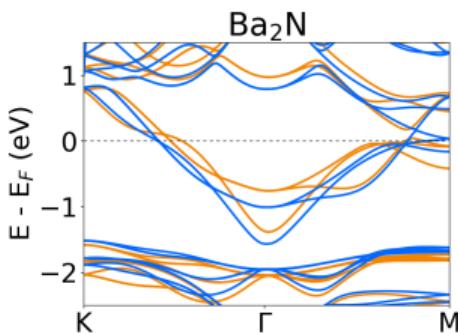
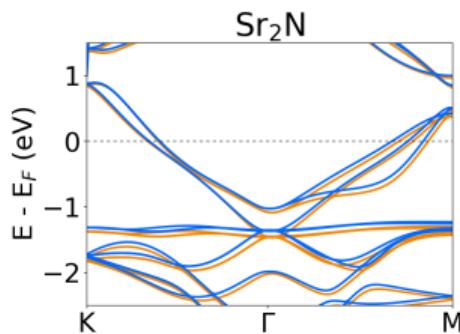
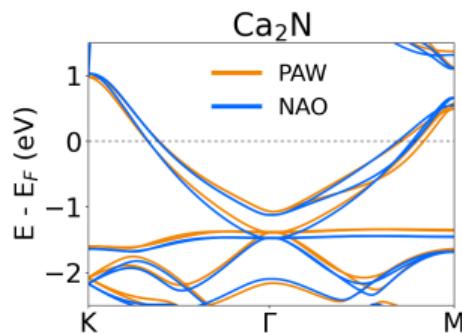


NAO Radial Wavefunction



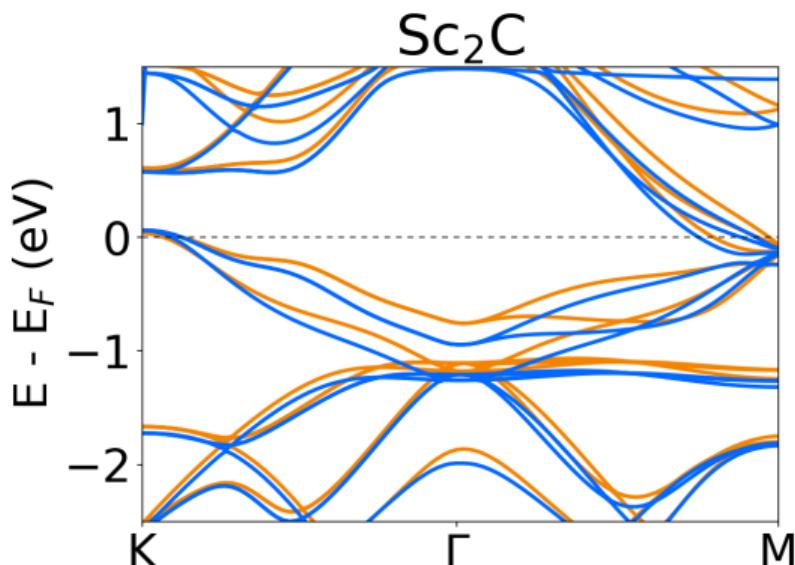
Projector-augmented wave (PAW) bases use planewaves in the regions away from nuclei, so all space is captured by basis functions. Numerical atom-centered orbital (NAO) bases have a finite radial extent, controlled by a cutoff potential. They may struggle to model non-atom-centered features...

Agreement of Basis Sets

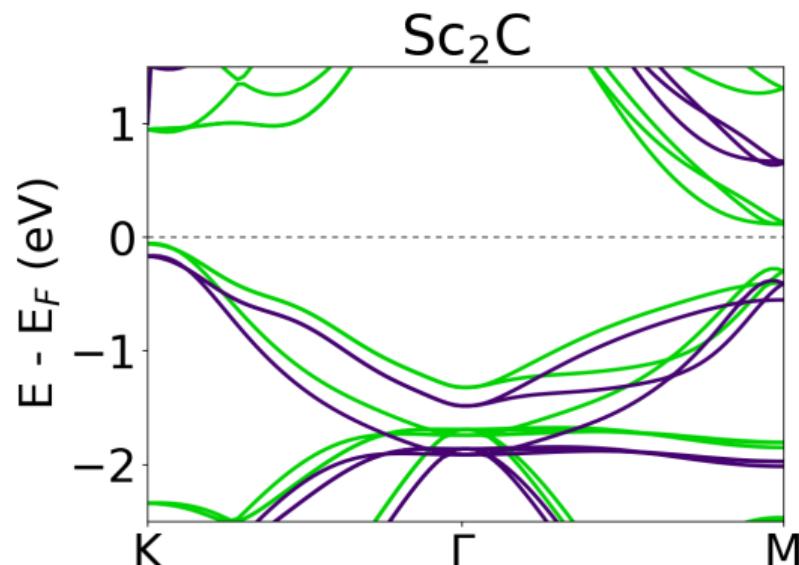


A Note on Sc_2C

Sc_2C is a small band-gap semiconductor, and GGA functionals tend to shrink band gaps.



Orange: B86bPBE-XDM/PAW
Blue: B86bPBE-XDM/NAO



Green: HSE06-XDM/NAO
Purple: PBE0-XDM/NAO

How do we account for thermal effects?

Most thermal effects in a crystal present as vibrations (phonons).

These can be modeled explicitly (quasi-harmonic approximation)

OR

They can be modeled approximately (Debye approximation)

Suppose that the phonon density of states has a simple form:

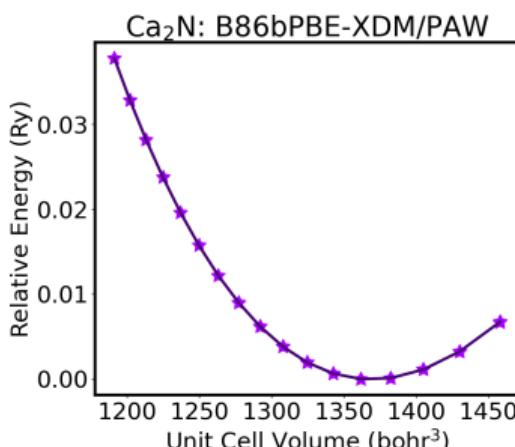
$$g_D(\omega) = \frac{9N\omega^2}{\omega_D^3}, \quad \omega < \omega_D \qquad 3N = \int_0^{\omega_D} g_D(\omega) d\omega$$

ω_D is the *Debye frequency*, which corresponds to the maximum phonon frequency in the system. The Debye model also assumes that all phonon frequencies are acoustic.

$$\omega = |\mathbf{k}|v_s$$

Employing the Debye Model

Attain a volume-energy curve for a solid:



The Debye temperature ($\Theta_D = \hbar\omega_D/k_B$) can be approximated as a function of the unit-cell volume and the static Bulk modulus ($B_{\text{sta.}}$).

$$\Theta_D(V) = \frac{f(1/4)}{k_B} \sqrt[3]{6\pi^2 n V^{\frac{1}{2}}} \sqrt{\frac{B_{\text{sta.}}}{M}}$$

The vibrational Helmholtz free energy (F_{vib}) can then be written as a function of Θ_D .

$$F_{\text{vib}} = nk_B T \left(\frac{9}{8} \frac{\Theta_D}{T} + 3 \ln \left(1 - e^{-\Theta_D/T} \right) - D_3 \left(\frac{\Theta_D}{T} \right) \right)$$

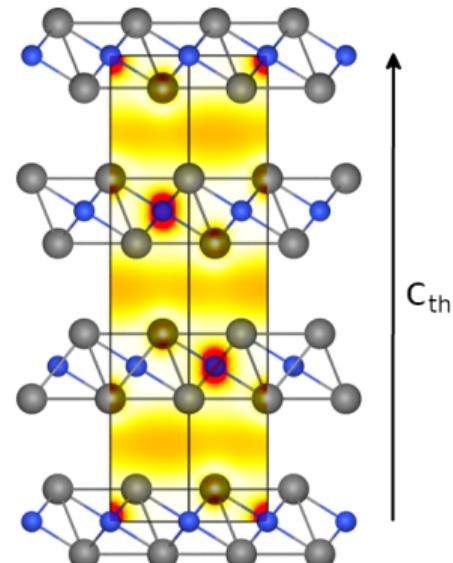
$$B_{\text{sta.}} = V \left(\frac{\partial^2 E}{\partial V^2} \right)$$

$$G(V, T) \approx E_{\text{elec}}(V) + F_{\text{vib}}(V, T)$$

Comparison to QHA

	c_{th}		V_{th}	
	Debye	QHA	Debye	QHA
%MAE (wrt QHA)	0.27	—	0.54	—
%MAE (wrt Expt)	1.82	1.91	3.48	3.34

Debye and QHA are in agreement. Both agree similarly compared to experiment.



c_{th} - c -parameter @ 298.15 K
 V_{th} - Cell volume @ 298.15 K

Accuracy of Methods

c_0, V_0 : c -parameter and cell volume @ 0 K

$c_{\text{th}}, V_{\text{th}}$: c -parameter and cell volume @ 298.15 K

Method	Basis	%MAE			
		c_0	c_{th}	V_0	V_{th}
B86bPBE-XDM	PAW	1.87	1.82	3.30	3.48
B86bPBE-XDM	NAO	2.06	2.13	4.65	4.70
PBE-XDM	PAW	2.06	2.13	4.90	4.97
PBE-XDM	NAO	2.29	2.30	5.15	5.15
PBE-D3BJ	PAW	2.28	2.51	3.23	3.58
PBE-D3	PAW	2.90	3.16	4.02	4.28
PBE-MBD-NL	NAO	2.25	2.31	5.09	5.15
PBE-TS	NAO	3.09	3.06	6.67	6.56

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The choice of an rigorous dispersion correction improves the accuracy of the predicted geometry.

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The small difference between the static and thermally expanded geometries tell us that thermal expansion is very minimal.

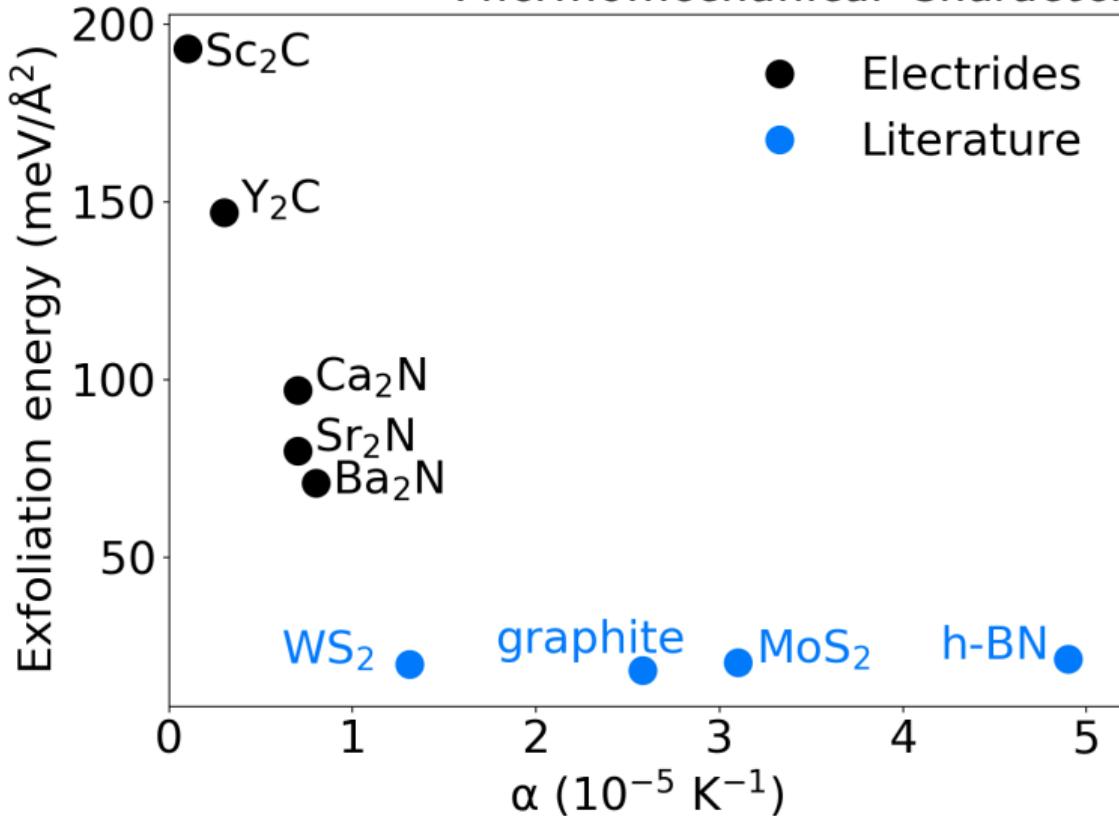
Exfoliation Energies

Computed with B86bPBE-XDM/PAW:

Electride	$E_{\text{exfol}}^{\text{total}}$ (meV/Å ²)	Base	Dispersion
Ca ₂ N	97	63%	37%
Sr ₂ N	80	61%	39%
Ba ₂ N	71	55%	45%
Sc ₂ C	193	67%	33%
Y ₂ C	147	65%	35%

The majority of the interlayer attraction is from the base functional (i.e. electrostatic). Sc₂C and Y₂C have two anionic electrons, so have more base contribution. Larger, more polarizable atoms lead to a greater fraction of dispersion.

Thermomechanical Characteristics



Volumetric coefficient of thermal expansion

$$\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P$$

What They Do: Summary

- NAO and PAW basis sets both adequately model the electride state.
- The Debye model is sufficient to model the thermal expansion of layered electrides.
- B86bPBE-XDM/PAW and PBE-D3BJ/PAW were our best-performing methods.
- Thermal expansion is extremely minimal, so it can safely be neglected.
- The small thermal expansion and large exfoliation energies make layered electrides unique among layered materials.

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2D Semiconductors
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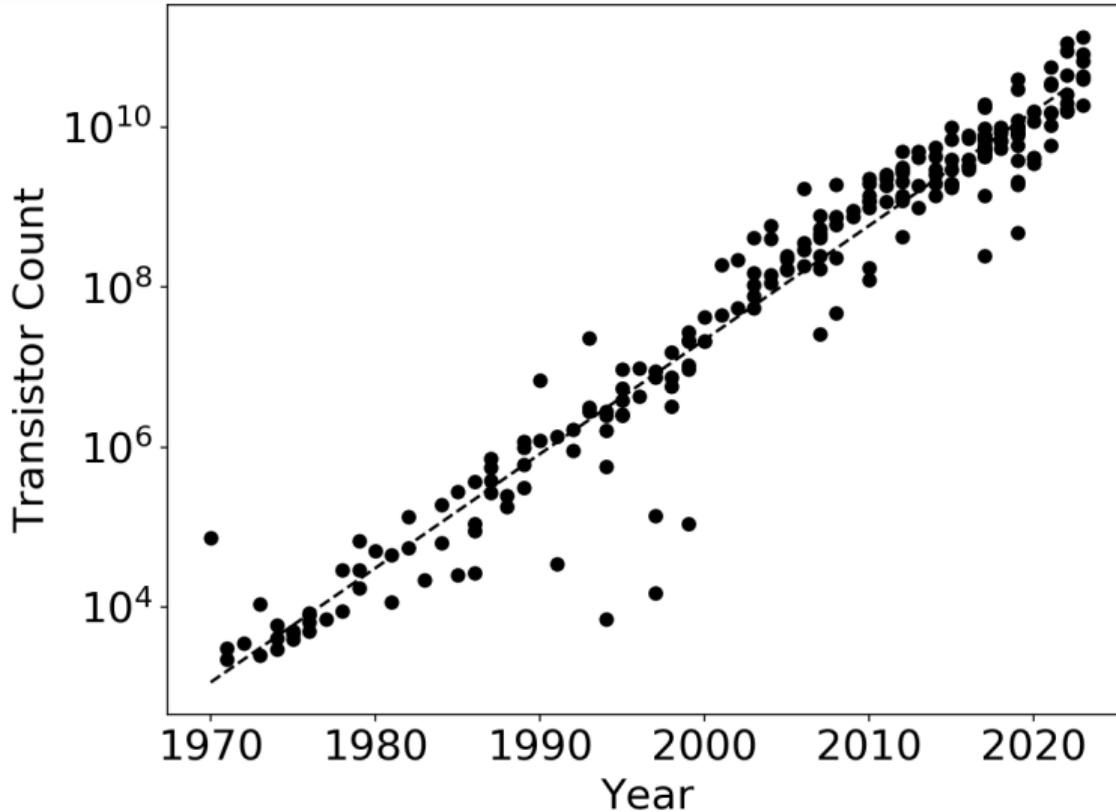
Conclusions
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Introduction

Thermal Expansion

2D Semiconductors

Conclusions



The Death of Moore's Law

Moore's law applies to silicon-based transistors.

Pivoting to a new material may be one of the greatest logistical challenges the semiconductor industry will face.

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A promising alternative to silicon are the transition metal dichalcogenides (TMDCs)

- They feature high mobility, short channel lengths, high on/off ratio, and a small subthreshold swing.

The Death of Moore's Law

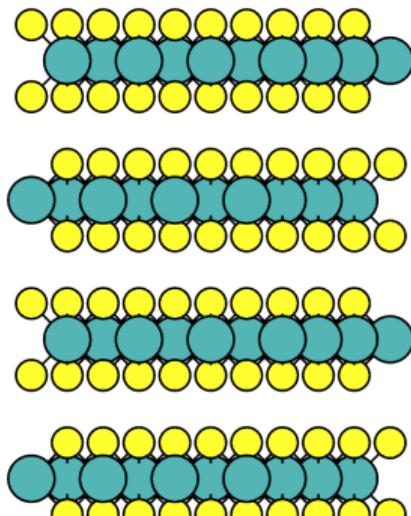
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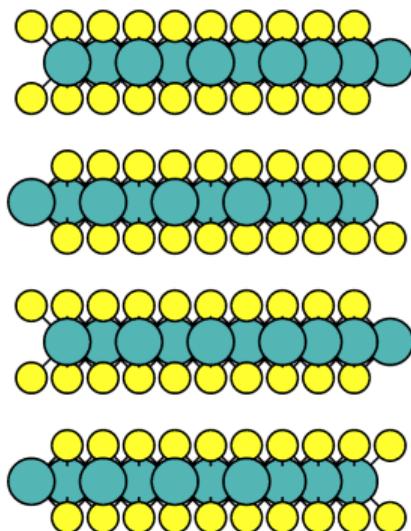
At the front of this class of materials is MoS_2 .



Bulk 2H-MoS₂

Molybdenum Disulfide

- First isolated in 2010.
- Observed in a variety of phases:
 - 1T, 1T', 2H, 3R
- 1T and 1T' are metallic
- 2H and 3R have indirect band gaps.
- Monolayer MoS₂ (1H) has a direct band gap.



The Contact Resistance Problem

The interface of a metal and a monolayer TMDC tends to exhibit a high contact resistance, *circa* $1 \text{ k}\Omega \cdot \mu\text{m}$

This can be attributed to:

- Tunneling barriers
- Schottky barriers
- Fermi-level pinning
- Gap state formation
- Sheet resistivity

There is also the issue of semiconductor doping.

Metal/MoS₂ Junctions

There has been some computational research into the interface properties of the metal/MoS₂ junction.

Kang *et al.* studied Pd, In, Au, Ti, W, and Mo with LDA

Gong *et al.* studied Al, Ag, Ir, Au, Pd, and Pt with LDA+D2

The local density approximation (LDA) already has a tendency to overbind and capture pseudo-dispersion, so its use and the addition of a dispersion correction is will not generally lead to accurate results.

However, both studies noted variance in the interface properties depending on the metal.

Kang *et al.*, Phys. Rev. X, 2014, 4, 031005.

Gong *et al.*, Nano Lett., 2014, 14, 1714.

Pn/MoS₂ Junctions

Heavy pnicogen semimetals (Sb, Bi) may be well suited as contact materials for TMDC-based devices.

They have a minimal DOS near the Fermi level, which is unlikely to cause a Schottky barrier.

Contact resistance values:

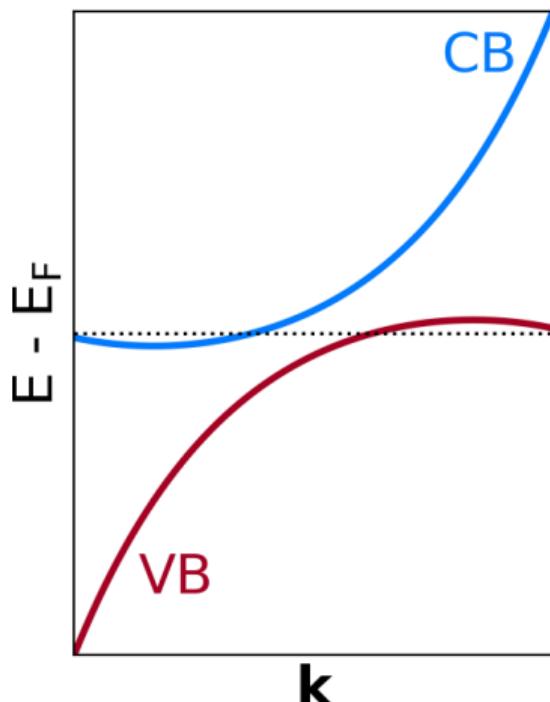
Bi(0001)¹: $123 \Omega \cdot \mu\text{m}$

Sb(0112)²: $42 \Omega \cdot \mu\text{m}$

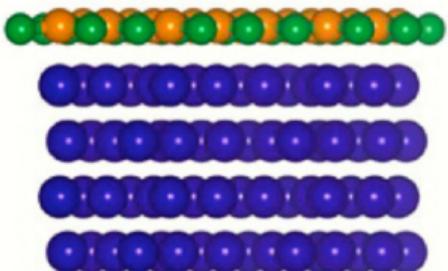
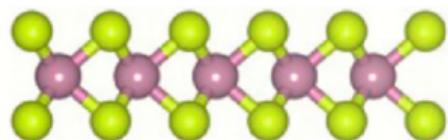
[1] Shen *et al.*, *Nature*, 2021, 593, 211.

[2] Li *et al.*, *Nature*, 2023, 613, 274.

Semimetal band structure:



Intermediate Materials



Co/h-BN/MoS₂

Insertion of a h-BN monolayer between a cobalt electrode and MoS₂ was shown to reduce the unfavourable chemical interactions that lead to high contact resistance.

However, this introduces a large tunneling barrier, leading to an experimentally observed contact resistance of $3 \text{ k}\Omega \cdot \mu\text{m}$.

Farmanbar and Brocks, *Phys. Rev. B*, **2015**, 91, 161304.

Wang et al., *Adv. Mater.*, **2016**, 28, 8302.

Cui et al., *Nano Lett.*, **2017**, 17, 4781.

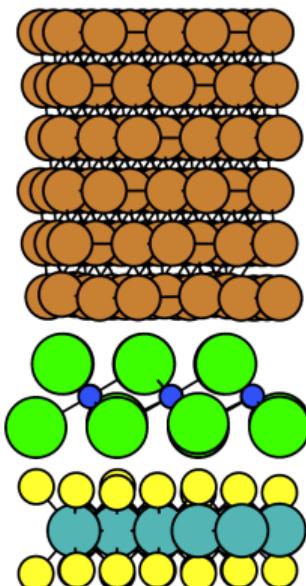
Electrenes as Intermediate Materials

Electrenes are an excellent material for this application!

- Tunneling barrier free
- Schottky barrier free
- n-doping MoS_2

Diznab *et al.* studied $\text{Au}/\text{AE}_2\text{Pn}/\text{MoS}_2$ and $\text{Cu}/\text{AE}_2\text{Pn}/\text{MoS}_2$ heterostructures for the predicted AE_2Pn electrides (Ca_2N , Sr_2N , Sr_2P , Ba_2N , Ba_2P , Ba_2As , Ba_2Sb)

They concluded that Ca_2N was the best overall choice, thanks to its large surface charge



The Next Question

Does the metal in a metal/Ca₂N/MoS₂ heterostructure affect the interface properties?

How does that compare to metal/MoS₂ heterostructures?

Geometry Metrics

Intermaterial Separation:

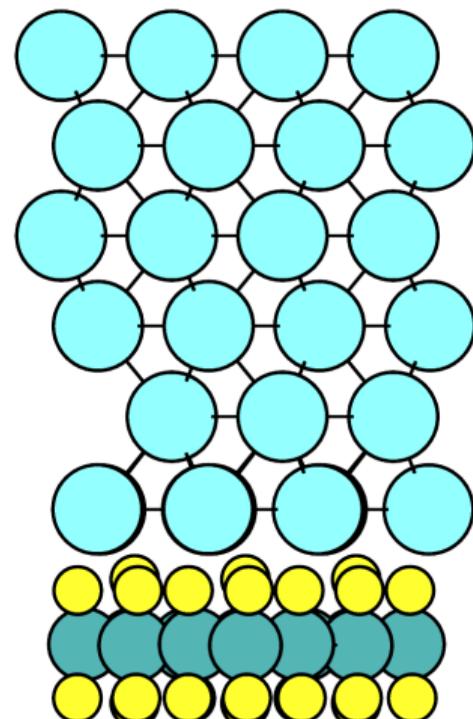
$$\Delta \bar{z}_{S\text{-metal}} = |\bar{z}_S - \bar{z}_{\text{metal}}|$$

The average z-distance between the contact sulfur of MoS₂ and the metal surface.

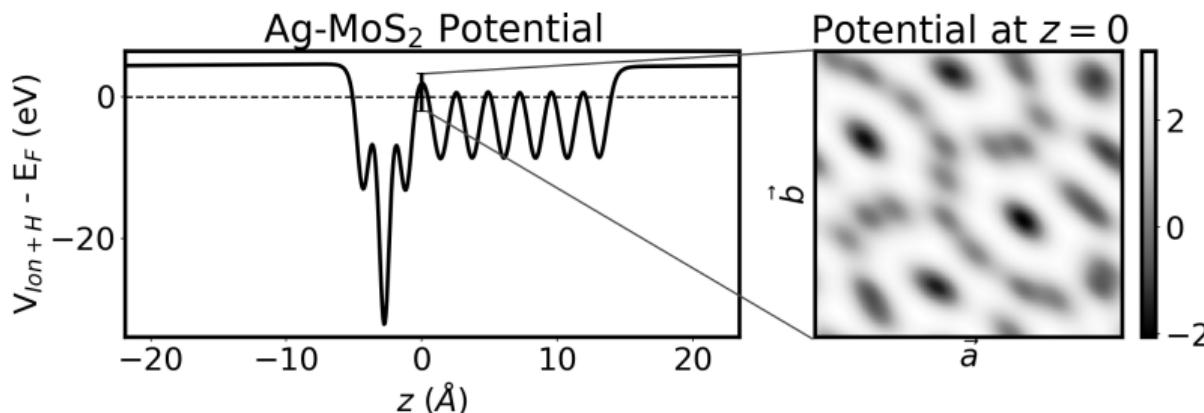
Interface Distortion:

$$\sigma_{S\text{-metal}} = \sqrt{\sigma_{z,S}^2 + \sigma_{z,\text{metal}}^2}$$

The standard deviation in $\Delta \bar{z}_{S\text{-metal}}$ representing the distortion at the interface.



Tunneling Metric



The electrostatic potential of a heterostructure is a 3D function. The xy -plane average at the metal/MoS₂ junction ($z = 0$) is defined as the tunneling barrier height (TBH).

Charge Transfer Metrics

Charge Transfer:

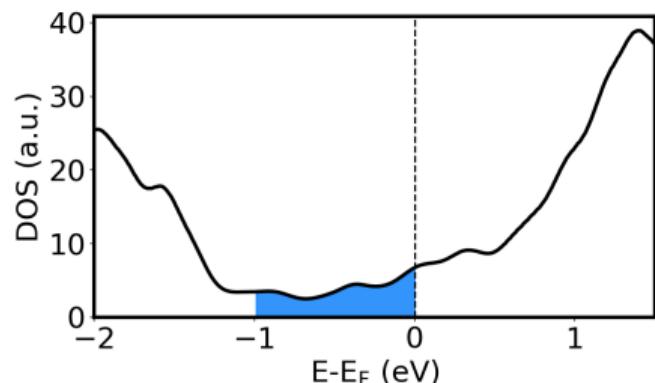
$$Q_{\text{MoS}_2} = Q_{\text{MoS}_2}^{\text{Heterostruc.}} - Q_{\text{MoS}_2}^{\text{Isolated}}$$

Net excess charge on each MoS_2 formula unit, computed in the QTAIM framework.

Integrated Gap States:

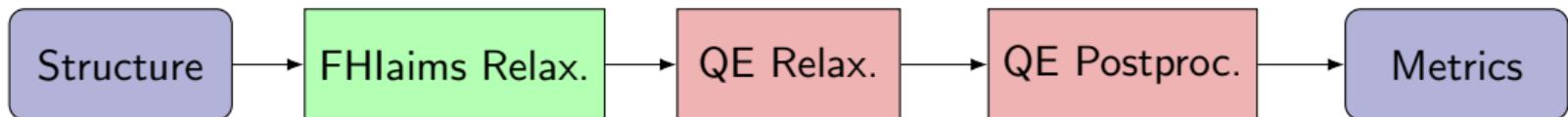
$$\text{IGS} = \frac{1}{A_{\text{cell}}} \int_{E_F - 1 \text{ eV}}^{E_F} D(E) \text{ d}E$$

An integral over the DOS from -1 to 0 eV relative to the Fermi level.



IGS, with the integral shown in blue.

Geometry Relaxation and Processing Method



PBE-XDM

FHIaims:

- lightdense basis set

Quantum ESPRESSO:

- 90.0 Ry energy cutoff
- 900.0 Ry density cutoff

Metal/MoS₂ Heterostructures: Bonding Type

Twelve metal/MoS₂ heterostructures were studied:

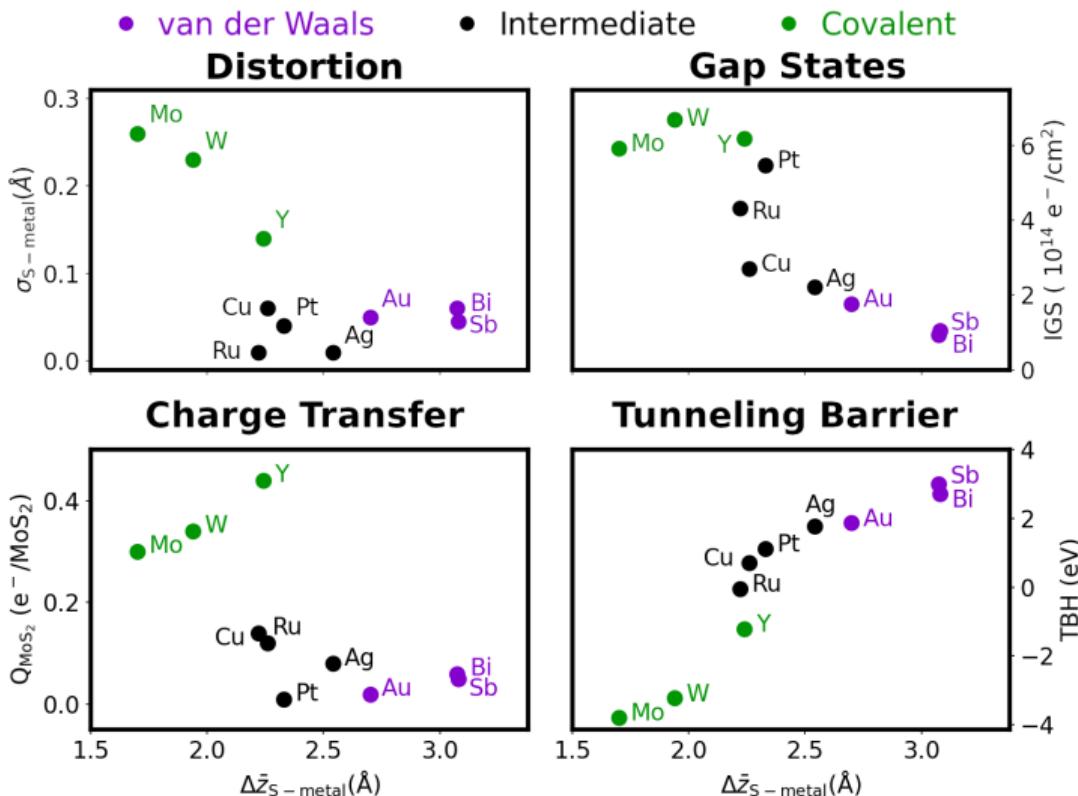
Sb(0001), Sb(011̄2), Bi(0001), Bi(011̄2), Au, Ag, Cu, Pt, Ru, Y, W, Mo

The type of bonding between the materials determines the interface characteristics

An indicator of the bonding type is the average z-distance

- Large Δz : van der Waals
- Medium Δz : intermediate
- Small Δz : covalent

Metal/MoS₂ Heterostructures: Metrics



Metal/MoS₂ Heterostructures: Takeaways

Metal/MoS₂ interactions can be classified on a vdW/covalent spectrum.

van der Waals

- Large Δz
- Small $\sigma_{\text{S-metal}}$
- Small $Q_{\text{MoS}2}$
- Small gap state formation
- Large tunneling barrier

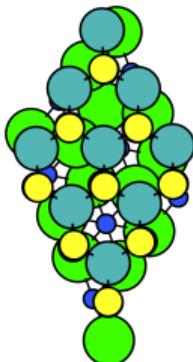
Covalent

- Small Δz
- Large $\sigma_{\text{S-metal}}$
- Large $Q_{\text{MoS}2}$
- Large gap state formation
- Small tunneling barrier

Ca₂N/MoS₂ Heterostructures

Geometry A Heterobilayer

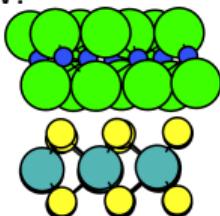
Top view:



Five Ca₂N/MoS₂ heterobilayers were considered:

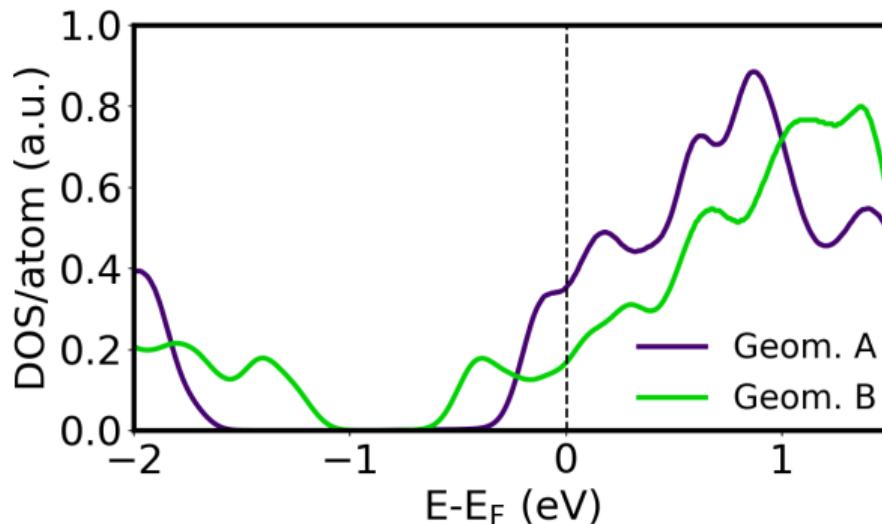
Geometry	N_{atoms}	$\varepsilon_{\text{Ca}_2\text{N}} (\%)$	$Q_{\text{MoS}_2} (\text{e}^-)$
Geom. A	48	0.14	0.35
Geom. B	21	1.67	0.35
Geom. C	87	2.35	0.35
Geom. D	105	4.20	0.36
Geom. E	66	5.23	0.34

Side view:



Ca₂N/MoS₂ Heterostructures: Band Gap Shrinking

Geometry	$E_{\text{Gap}}^{\text{MoS}_2}$ (eV)
Geom. A	1.3
Geom. B	0.5
Geom. C	0.9
Geom. D	0.7
Geom. E	0.6



The band gap of MoS₂ is sensitive to strain, but *no strain is applied to the MoS₂ structure.*

The Geometric Distortion

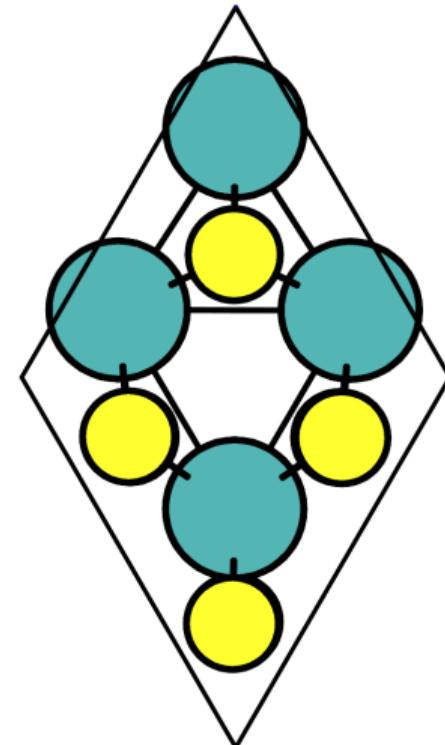
The shrunken band gap is retained when the Ca₂N is deleted from the structure.

This tells us that this originates from a geometric distortion!

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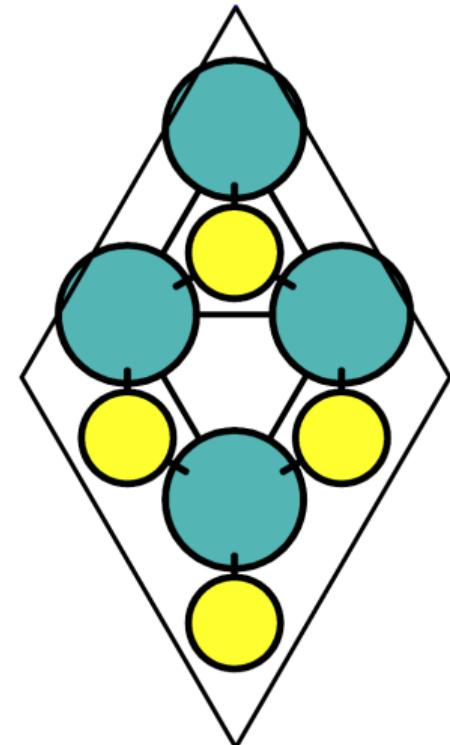
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The Geometric Distortion

The shrunken band gap is retained when the Ca_2N is deleted from the structure.

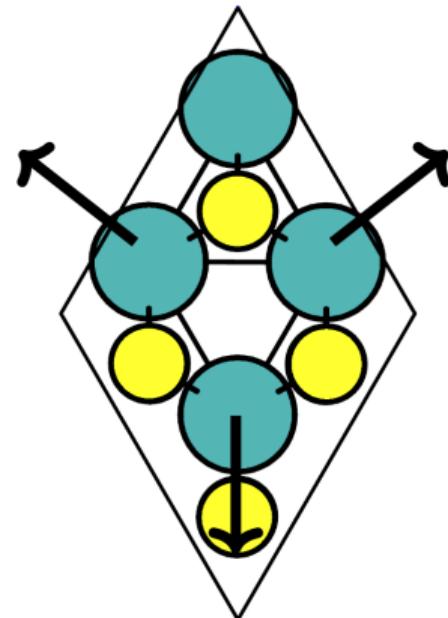
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The Geometric Distortion

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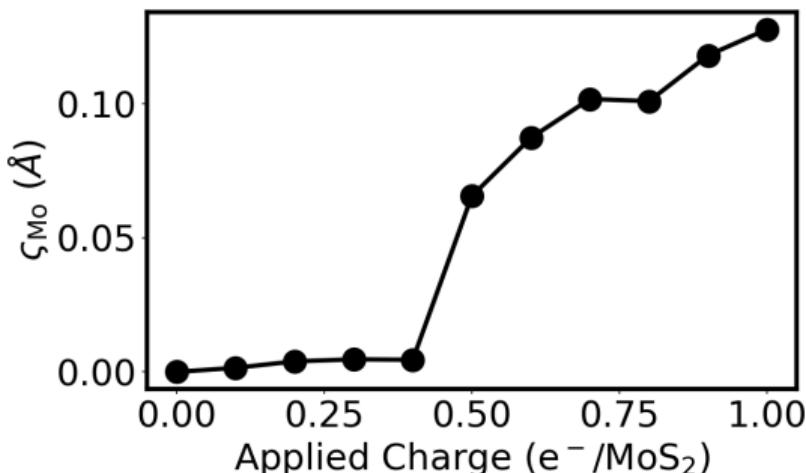
This tells us that this originates from a geometric distortion!



$$\varsigma_{\text{Mo}} = \sqrt{\frac{1}{N} \sum_i \left(d_i^{\text{Mo-Mo}} - d_{\text{pristine}}^{\text{Mo-Mo}} \right)^2}$$

The Origin(?) of Band Gap Shrinking

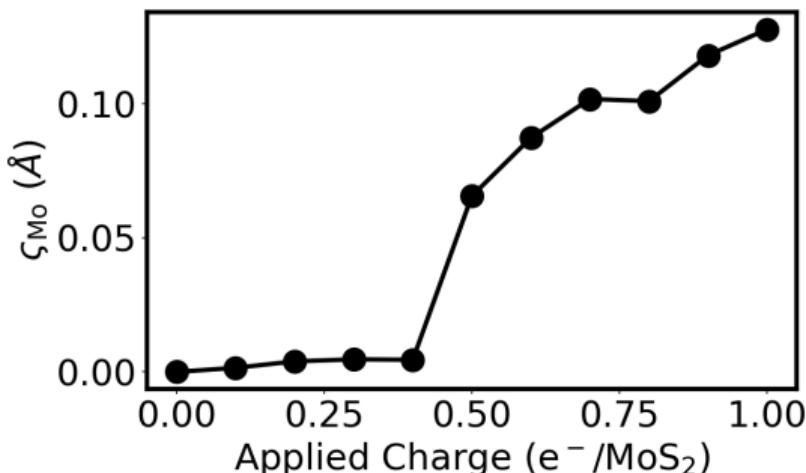
MoS₂ can favour the 1T' phase over 1H given excess negative charge.



MoS₂ spontaneously distorts *circa* 0.5 e^-/MoS_2

The Origin(?) of Band Gap Shrinking

MoS_2 can favour the 1T' phase over 1H given excess negative charge.



MoS_2 spontaneously distorts *circa* $0.5 e^-/\text{MoS}_2$

But that is *less* than all of the $\text{Ca}_2\text{N}/\text{MoS}_2$ Geometries! ($0.35 e^-/\text{MoS}_2$)

ς_{Mo} for Metal/MoS₂

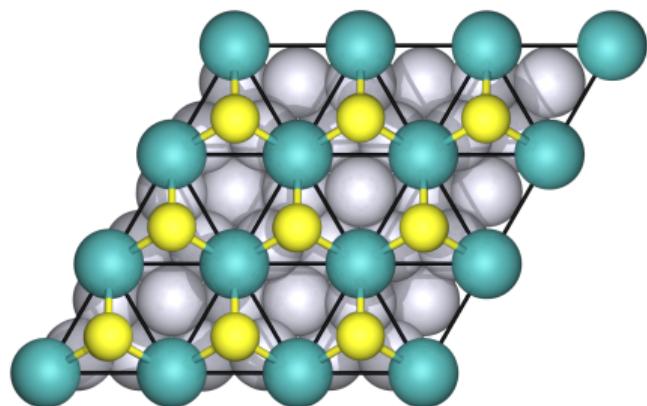
Metal/MoS ₂	ς_{Mo} (Å)	Q_{MoS_2} (e ⁻ /MoS ₂)
Sb(0001)/MoS ₂	0.00	0.04
Sb(011̄2)/MoS ₂	0.00	0.06
Bi(0001)/MoS ₂	0.03	0.02
Bi(011̄2)/MoS ₂	0.00	0.08
Au/MoS ₂	0.00	0.02
Ag/MoS ₂	0.00	0.08
Cu/MoS ₂	0.01	0.12
Pt/MoS ₂	0.00	0.01
Ru/MoS ₂	0.01	0.14
Y/MoS ₂	0.18	0.44
W/MoS ₂	0.04	0.34
Mo/MoS ₂	0.03	0.30

For most metal/MoS₂ interfaces, ς_{Mo} is small.

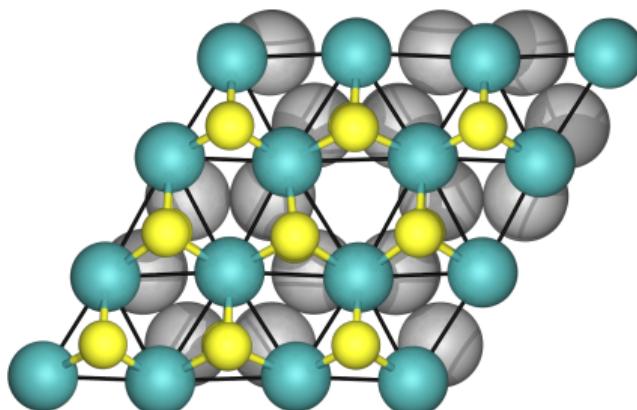
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Sb(011̄2)/MoS ₂	0.00	0.06	
Bi(0001)/MoS ₂	0.03	0.02	For most metal/MoS ₂ interfaces, ς_{Mo} is small.
Bi(011̄2)/MoS ₂	0.00	0.08	
Au/MoS ₂	0.00	0.02	
Ag/MoS ₂	0.00	0.08	Only Y/MoS ₂ has a large ς_{Mo} .
Cu/MoS ₂	0.01	0.12	The isolated, distorted MoS ₂ from that interface also has a shrunken band gap.
Pt/MoS ₂	0.00	0.01	
Ru/MoS ₂	0.01	0.14	
Y/MoS ₂	0.18	0.44	
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Symmetry Breaking



Pt/MoS₂



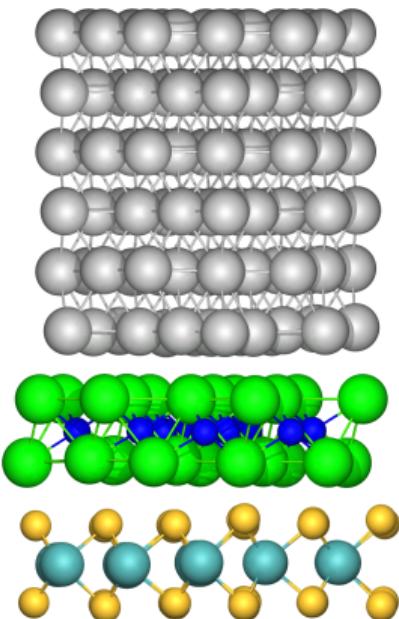
Y/MoS₂

MoS₂ conforms to the top layer of Yttrium atoms. Large charge transfer may permit this effect.

The same symmetry breaking is observed in Ca₂N/MoS₂ Geometries B-E.

Metal/Ca₂N/MoS₂ Heterostructures

How does the insertion of a Ca₂N monolayer affect the metal/MoS₂ junction?

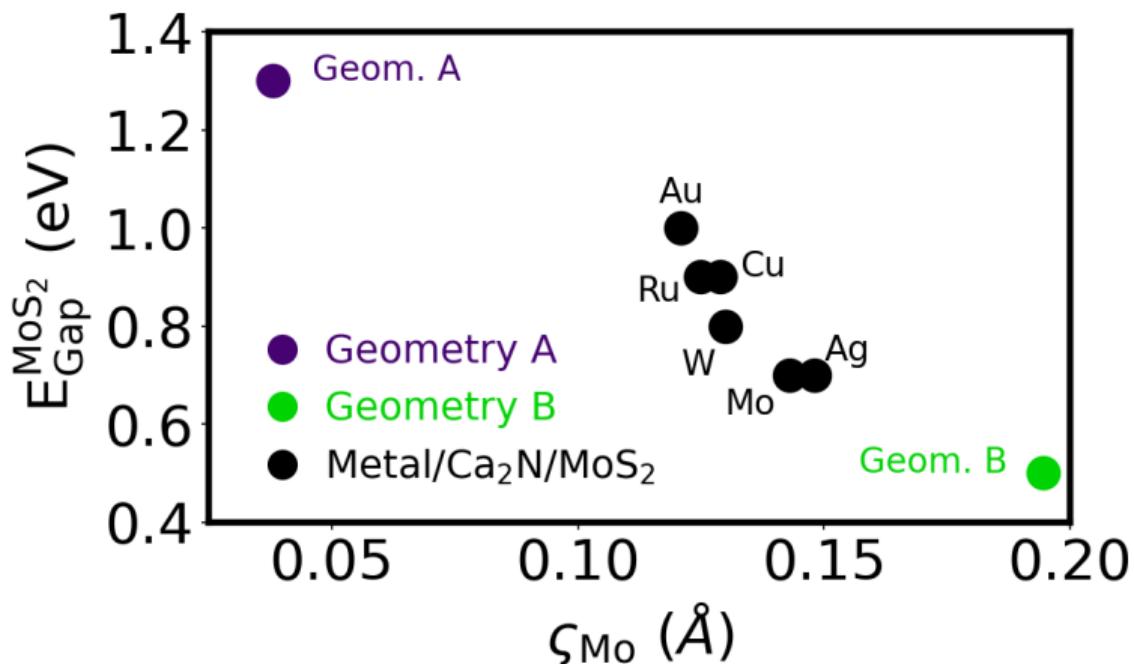


Six metals were considered:
Cu, Ag, Au, Ru, Mo, W

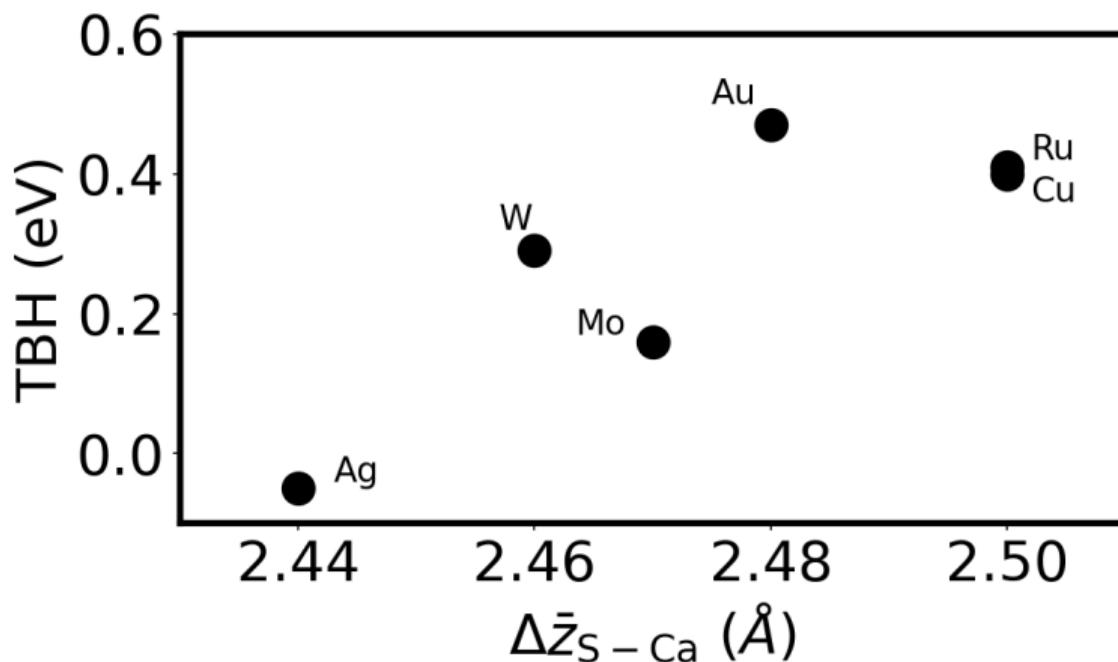
Things to look out for:

- SMo distortion
- Creation of a tunneling barrier
- Variability of metrics w.r.t. metal species

Metal/Ca₂N/MoS₂ Heterostructures: ζ_{Mo}



Metal/Ca₂N/MoS₂ Heterostructures: Tunneling Barrier Heights



Standard Deviations of Metrics

$$\sigma = \sqrt{\frac{1}{N} \sum_i (X_i - \bar{X})^2}$$

Interface	Standard Deviation			
	Δz (Å)	$\sigma_{S\text{-metal}}$ (Å)	Q_{MoS_2} (e ⁻ /MoS ₂)	TBH (eV)
Metal/MoS ₂	0.37	0.11	0.13	2.48
Metal/Ca ₂ N/MoS ₂	0.02	<0.01	0.02	0.20

($N = 6$)

Compared to Metal/MoS₂, Metal/Ca₂N/MoS₂ interface metrics are only weakly influenced by the choice of the metal.

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LAYERED ELECTRIDES

WHAT THEY ARE:

WHAT THEY DO:

WHAT CAN THEY DO:

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- Ionic materials where a localized electron acts as an anion
- 0D, 1D, 2D, 3D
- Electrenes are 2D electride monolayers

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WHAT CAN THEY DO:

- Enable low resistance contacts to 2D semiconductors
- Introduce flexibility in the choice of metals for those junctions