

Introduction
oooooooooooo

Electrides
oooooooo

Interfaces
oooooooo

Future Work
oooo

QUALIFYING REPORT:

DFT Calculations on Exotic Layered Materials and their Applications

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April 18th, 2024

Acknowledgements

Prof. Erin Johnson
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Prof. Saraubh Chitnis
Prof. Ryan MacDonell
Prof. Jesse Maassen

Prof. Carlie Charron



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Introduction
oooooooooooo

Electrides
oooooooo

Interfaces
oooooooo

Future Work
oooo

Introduction

Electrides

Interfaces

Future Work

Introduction
oooooooooooo

Electrides
oooooooo

Interfaces
oooooooo

Future Work
oooo

Introduction

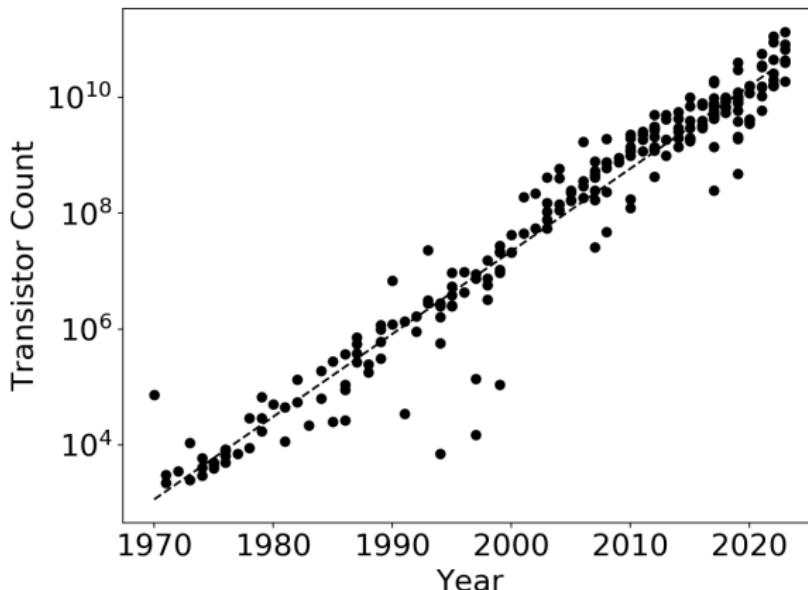
Electrides

Interfaces

Future Work

Gordon Moore's Prediction

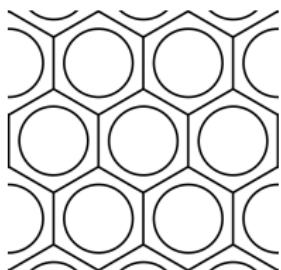
The number of transistors on an integrated circuit will double every two years.



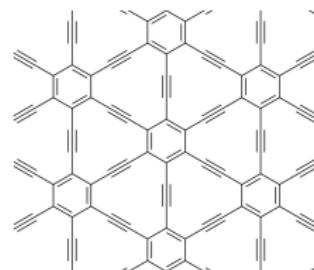
¹ Transistor Count. Wikipedia. 2024.

The 2D Revolution

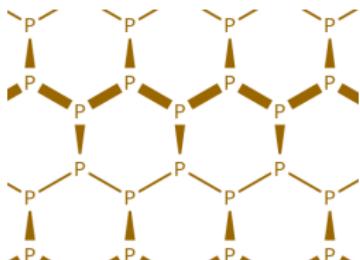
Materials composed of many stacked atomic layers, bound together by dispersion interactions, may be exfoliated to their monolayers.



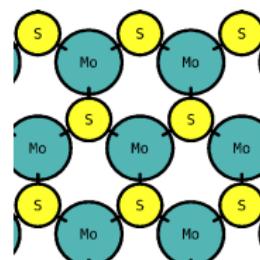
Graphene



Graphyne



Black Phosphorus

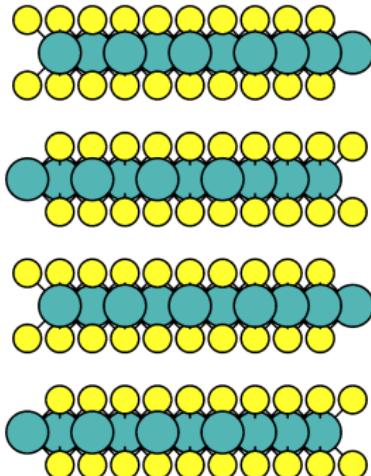


2H-MoS₂

Molybdenum Disulfide (MoS_2)

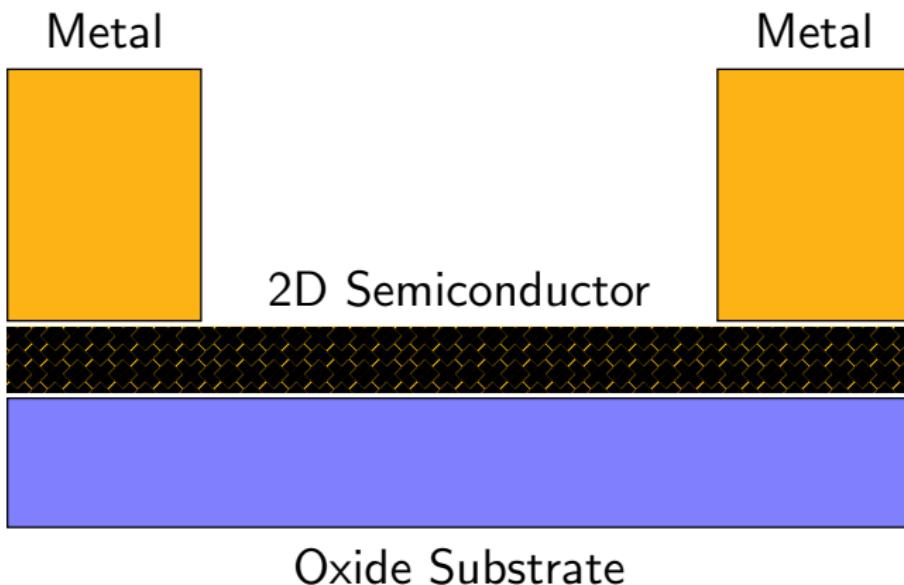
- Member of the transition metal dichalcogenides
- First isolated in 2012
- Two phases: 2H and 1T
- Bulk: indirect band gap semiconductor
- Monolayer: direct band gap semiconductor

Very appealing for monolayer semiconductor devices.



²Phys Rev. Lett. 105, 136805 (2010).

Monolayer Semiconductor Transistors



The Contact Resistance Problem

Metal contacts with TMDCs tend to have very high contact resistance.

This effect can be attributed to a lack of dangling bonds and leads to a combination of:

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

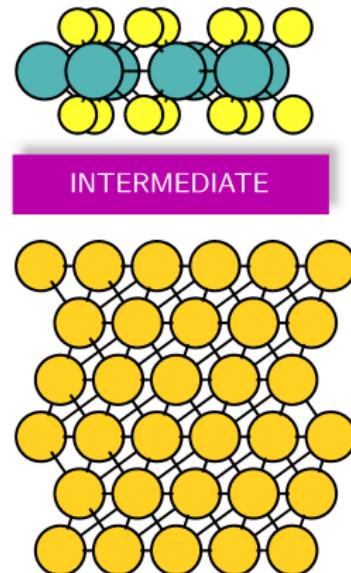
Semiconductor doping has to be accomplished by different methods.

Can Intermediate Materials Resolve the Contact Resistance Problem?

A monolayer of hexagonal boron nitride has been shown to lower contact resistance across a Co–MoS₂ junction.

An electron-rich monolayer between the metal and the MoS₂ could:

- Inject charge into the semiconductor
- Promote a low-contact resistance junction
- Minimize tunneling effects



³Phys. Rev. B **91**, 161304 (2015).

Electrides

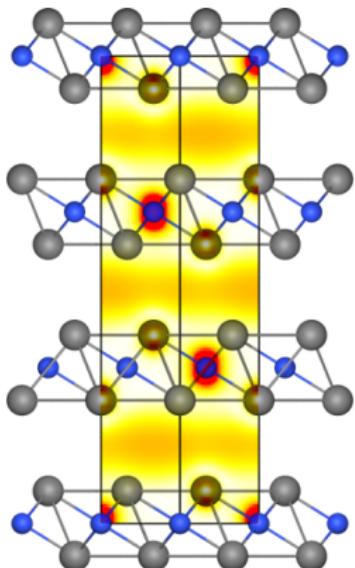
Ionic materials where the anion is an electron localized inside voids.

Of interest for their low work functions and high electron mobility.
May be applied to chemical synthesis and catalysis, and to electronic devices that require facile electron transfer.

Dimensionality of the electride determined by the shape of the localized electron:

- 0D: point-like (Ca_3Pb)
- 1D: long channel ($\text{K}^+(\text{cryptand}-2.2.2)\text{e}^-$)
- 2D: sheets (Ca_2N)
- 3D: more complex ($[\text{Ca}_{24}\text{Al}_{28}\text{O}_{64}]^{4+}(4\text{e}^-)$)

Layered Electrides

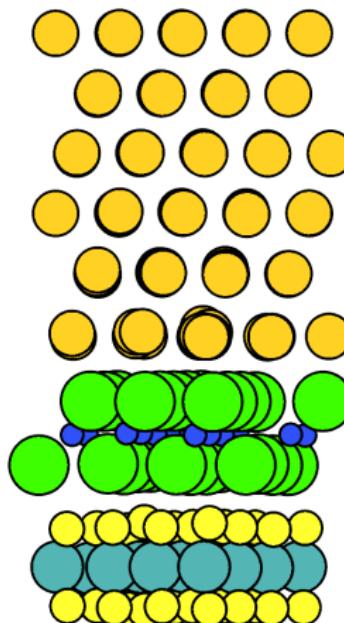


Yellow/orange regions between the layers represents the interstitial electron density

Electrons localized between thin, positively charged atomic sheets.

May be exfoliated to a monolayer where each side holds 0.5 e^- .

Metal–Ca₂N–MoS₂ Heterostructures



[AE₂Pn]⁺:e⁻ electrides as intermediates

What role does the metal play?

Hoc Opus

Does density-functional theory predict layered
electride geometries accurately compared to
experiment?

What are the interface properties of various metals
directly in contact with MoS₂?

Density-Functional Theory

$$E[\rho] = T + \int V_{\text{ext}}(\mathbf{r})\rho(\mathbf{r})d\mathbf{r} + J[\rho] + E_{\text{xc}}[\rho]$$

$$E_{\text{xc}} = E_X + E_C$$

$$E_X^{\text{GGA}} = - \sum_{\sigma} \int c_X \rho_{\sigma}^{4/3} F(\chi_{\sigma}) d\mathbf{r}$$

$$E_{\text{Total}} = E_{\text{DFT}} + E_{\text{Disp.}}$$

Disp. \sim XDM, D3(BJ), TS, MBD

Introduction
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Electrides
oooooooo

Interfaces
oooooooo

Future Work
oooo

Introduction

Electrides

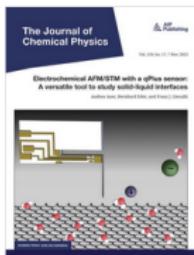
Interfaces

Future Work



Volume 159, Issue 17

7 November 2023



RESEARCH ARTICLE | NOVEMBER 01 2023

Low thermal expansion of layered electrides predicted by density-functional theory

Special Collection: John Perdew Festschrift

Adrian F. Rumson ; Erin R. Johnson

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Author & Article Information

J. Chem. Phys. 159, 174701 (2023)

<https://doi.org/10.1063/5.0171959> Article history

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Layered electrides are a unique class of materials with anionic electrons bound in interstitial regions between thin, positively charged atomic layers. While density-functional theory is the tool of choice for computational study of electrides, there has to date been no systematic comparison of density functionals or dispersion corrections for their accurate simulation. There has also been no research into the thermomechanical properties of layered electrides, with computational predictions considering only static lattices. In this work, we investigate the thermomechanical properties of five layered electrides using density-functional theory to evaluate the magnitude of thermal effects on their lattice constants and cell volumes. We also assess the accuracy of five popular dispersion corrections with both planewave and numerical atomic orbital calculations.

Topics

[Numerical atomic orbitals](#), [Density functional theory](#), [Phonons](#), [Electronic band structure](#),
[Debye model](#), [Quasi-harmonic approximation](#), [2D materials](#), [Thermal effects](#)



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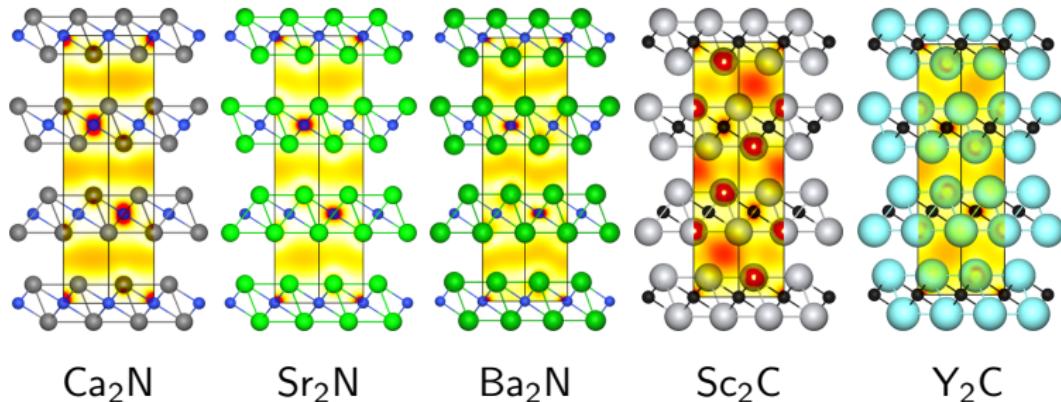


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The Plan

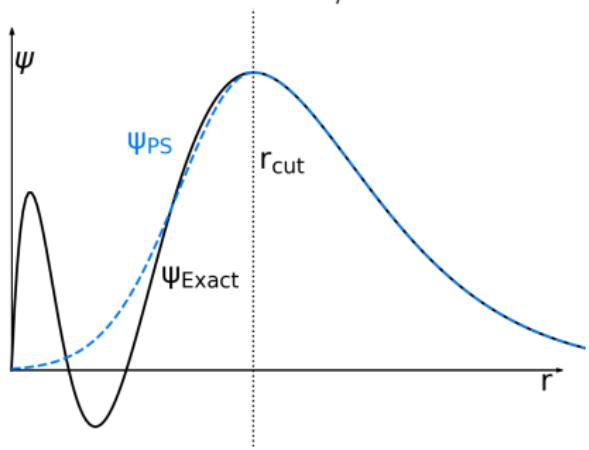


Compare various DFT predicted geometries to experimental XRD data collected at room temperature.

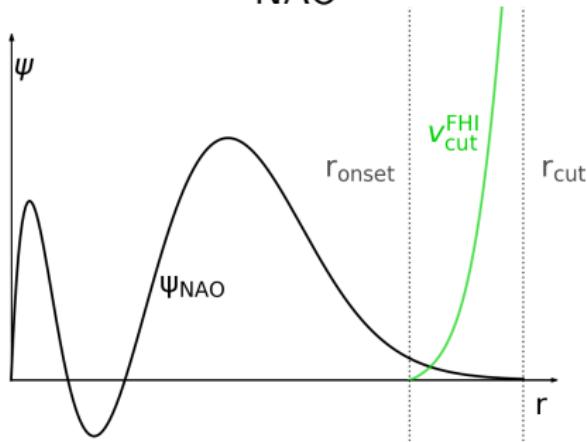
Explore planewave/PAW vs NAO basis sets, and dispersion corrections (XDM, D3, D3BJ, MBD, TS).

PAW vs. NAO

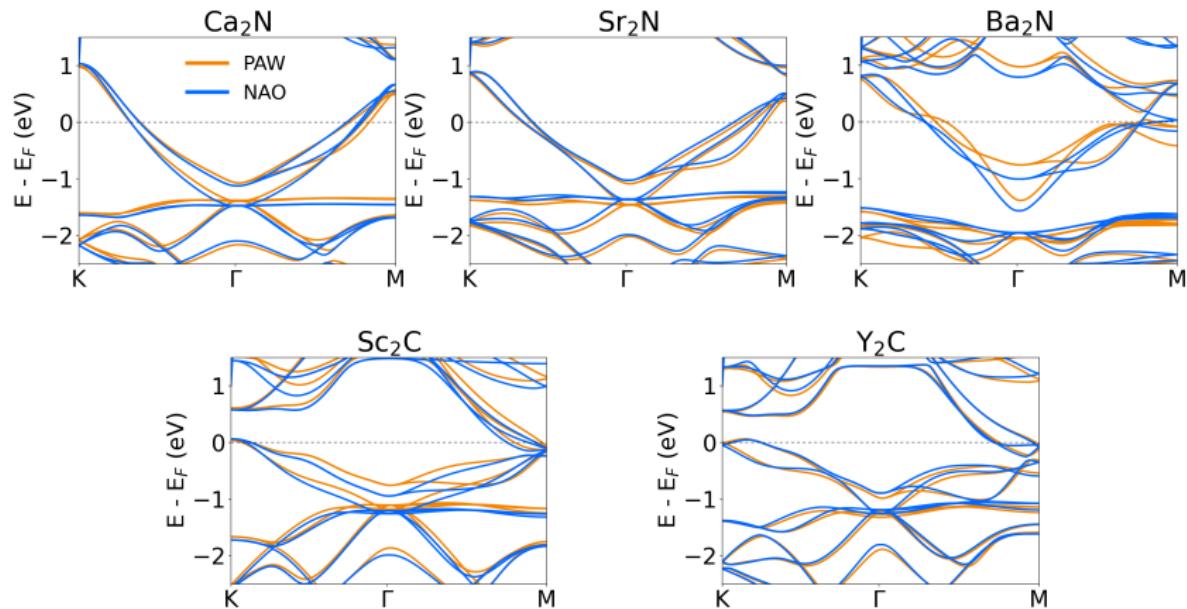
Planewave/PAW



NAO



Electronic Structure



The Debye Approximation

$$G(V, T) = F(V, T) = E_{\text{el}}(V) + F_{\text{vib}}(V, T)$$

$$F_{\text{vib}} = \int_0^{\infty} \left[\frac{\omega}{2} + k_B T \ln \left(1 - e^{-\omega/k_B T} \right) \right] g_D(\omega) d\omega$$

$$g_D(\omega) = \begin{cases} \frac{9N\omega^2}{\omega_D^3} & \text{if } \omega < \omega_D \\ 0 & \text{if } \omega \geq \omega_D \end{cases}$$

$$\int_0^{\omega_D} g_D(\omega) d\omega = 3N$$

Allow us to predict the thermally expanded volume (which minimizes G at some T).

Accuracy of Methods

$$\%MAE(V^{\text{pred.}}) = \left(\frac{1}{V^{\text{expt.}}} \sum_i \frac{|V_i^{\text{pred.}} - V_i^{\text{expt.}}|}{N} \right) \times 100\%$$

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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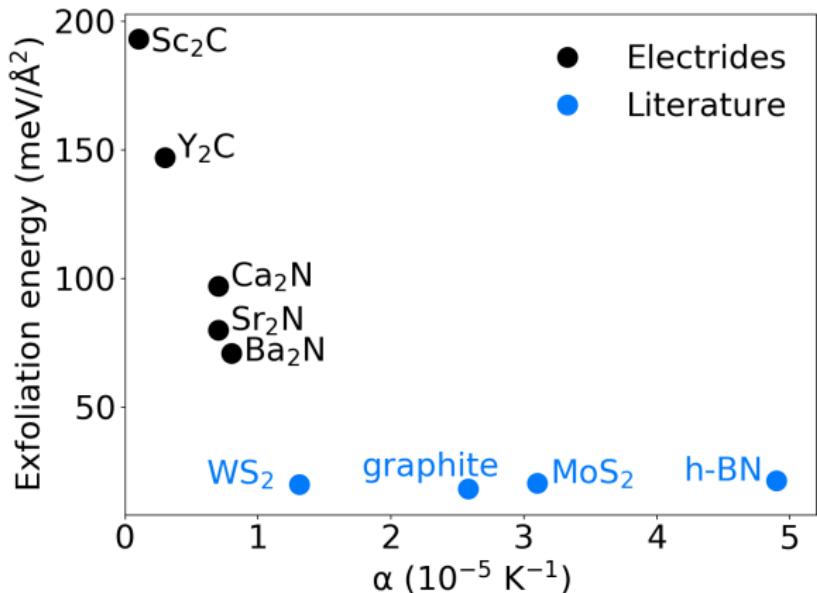
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Thermomechanical Characteristics



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

Conclusions

- NAO and PAW basis sets are in agreement.
- PAW/B86bPBE-XDM and PAW/PBE-D3BJ are the most accurate at predicting experimental geometries.
- Layered electrides exhibit very minimal thermal expansion and very large exfoliation energies.
- Minimal accuracy is gained by adding thermal effects to the DFT relaxation of layered electrides.

Introduction
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Electrides
oooooooo

Interfaces
oooooooo

Future Work
oooo

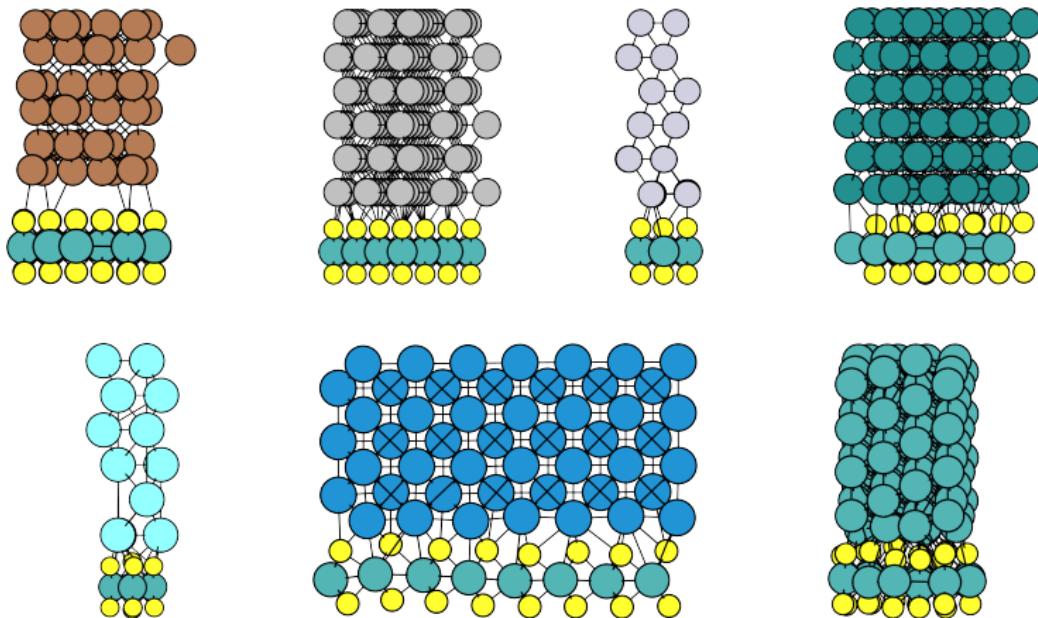
Introduction

Electrides

Interfaces

Future Work

Metal-MoS₂ Interfaces

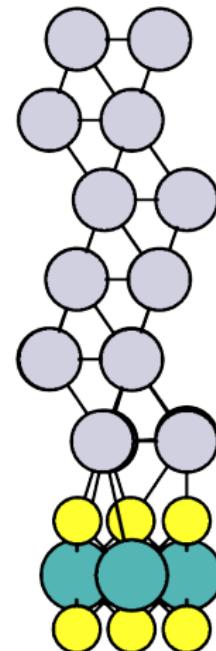


⁴Rafiee Diznab, M. et al. Designing Barrier-Free Metal/MoS₂ Contacts through Electrene Insertion. Accepted.

Properties for Analysis

- Inter-material separation: $\Delta\bar{z}_{S\text{-metal}}$
- Distortion at the interface: $\sigma(\Delta z_{S\text{-metal}})$
- Bader charge transfer: $Q_{\text{Bader}}^{\text{MoS}_2}$
- Exfoliation energy: $E_{\text{exfol.}}$
- Tunneling barriers: TBH, TBW
- Gap state formation

Tell us about whether the interface bonding is
covalent or van der Waals.



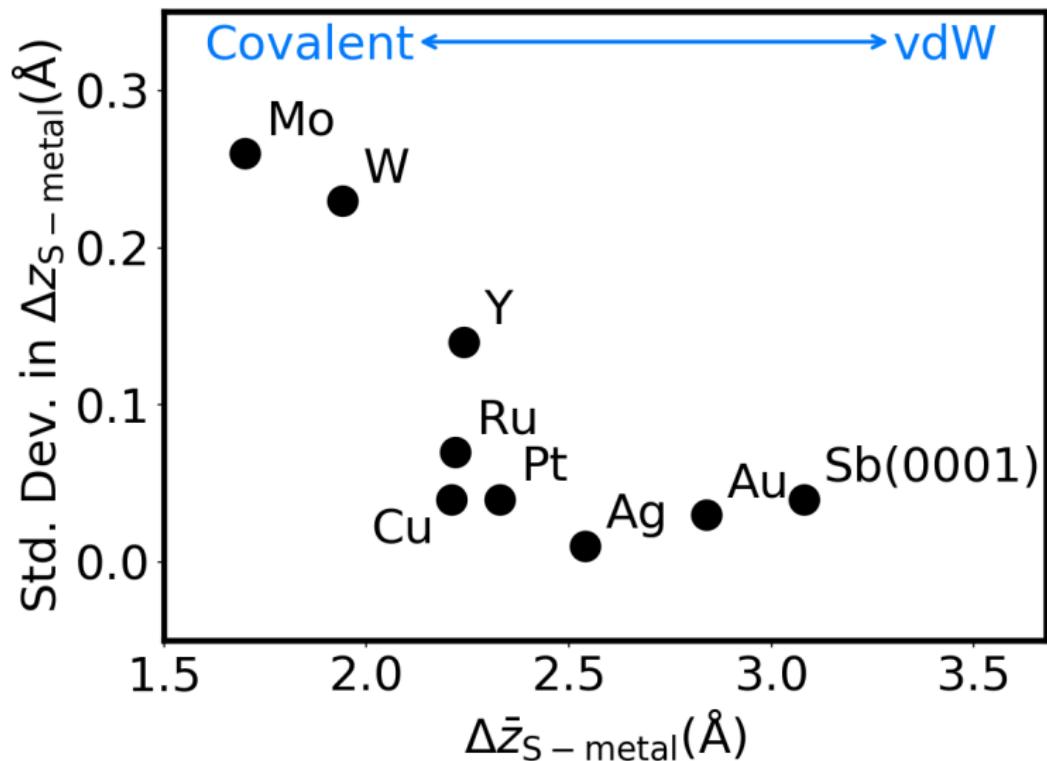
Introduction
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Electrides
oooooooo

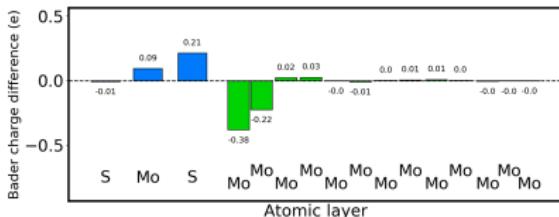
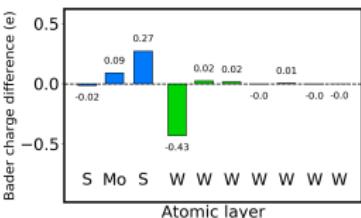
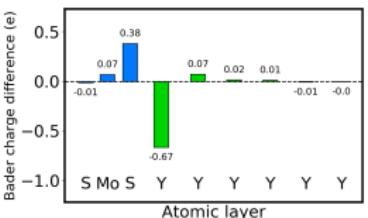
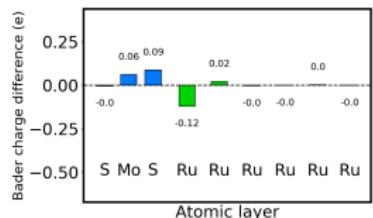
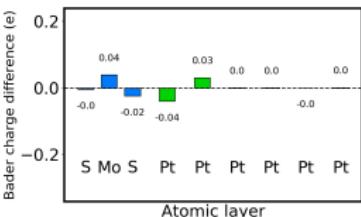
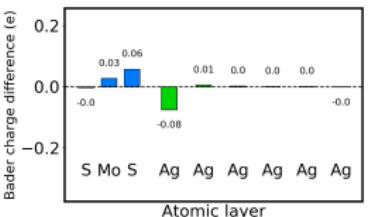
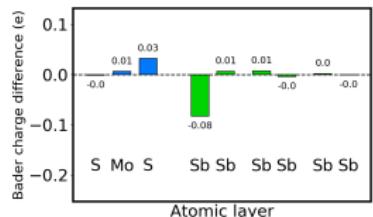
Interfaces
oo●oooo

Future Work
oooo

Heterostructure Geometry



Bader Charge Transfer



Bader Charge Transfer

Metal	$Q_{\text{Bader}}^{\text{MoS}_2}$ (e)	$\Delta \bar{z}$ (Å)	W_{metal} (eV)
Sb(0001)	0.04	3.08 ± 0.04	4.55
Ag	0.08	2.54 ± 0.01	4.74
Pt	0.01	2.33 ± 0.04	5.64
Ru	0.14	2.22 ± 0.07	4.71
Y	0.44	2.24 ± 0.14	3.1
W	0.34	1.94 ± 0.23	4.63
Mo	0.30	1.70 ± 0.26	4.55

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Exfoliation Energy

$$E_{\text{exfol}}^{\text{str}} = E_{\text{exfol}}^{\text{SCF}} + E_{\text{exfol}}^{\text{disp}}$$

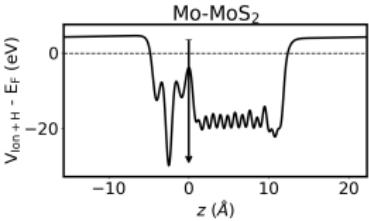
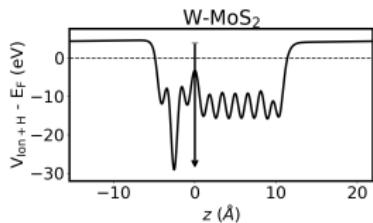
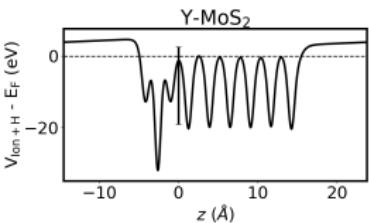
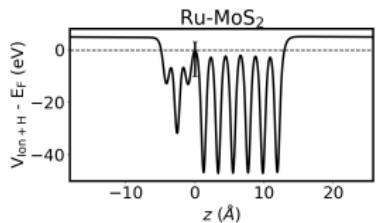
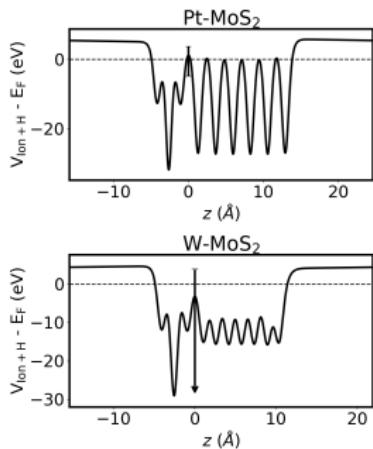
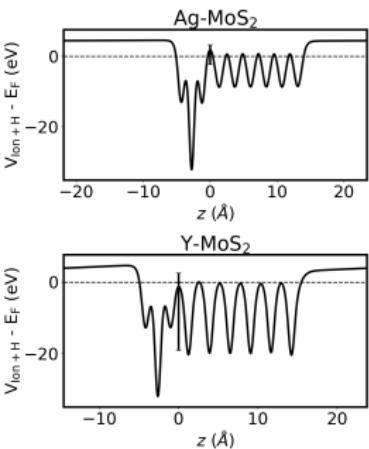
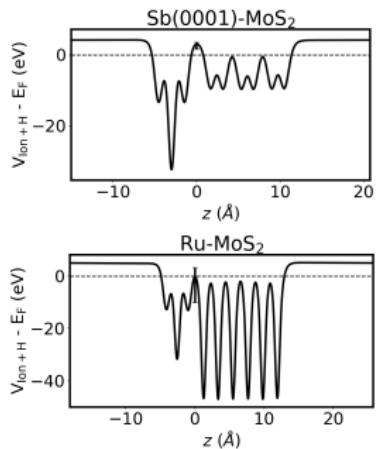
Metal	$Q_{\text{Bader}}^{\text{MoS}_2}$ (e)	$E_{\text{exfol}}^{\text{str}}$	$E_{\text{exfol}}^{\text{SCF}}$	$E_{\text{exfol}}^{\text{disp}}$
Sb(0001)	0.04	18.6	-4.7	23.3
Ag	0.08	121.1	84.0	37.1
Pt	0.01	59.1	8.0	51.1
Ru	0.14	95.4	36.4	59.0
Y	0.44	101.0	66.0	35.1
W	0.34			
Mo	0.30	85.6	31.0	54.6

Exfoliation Energy

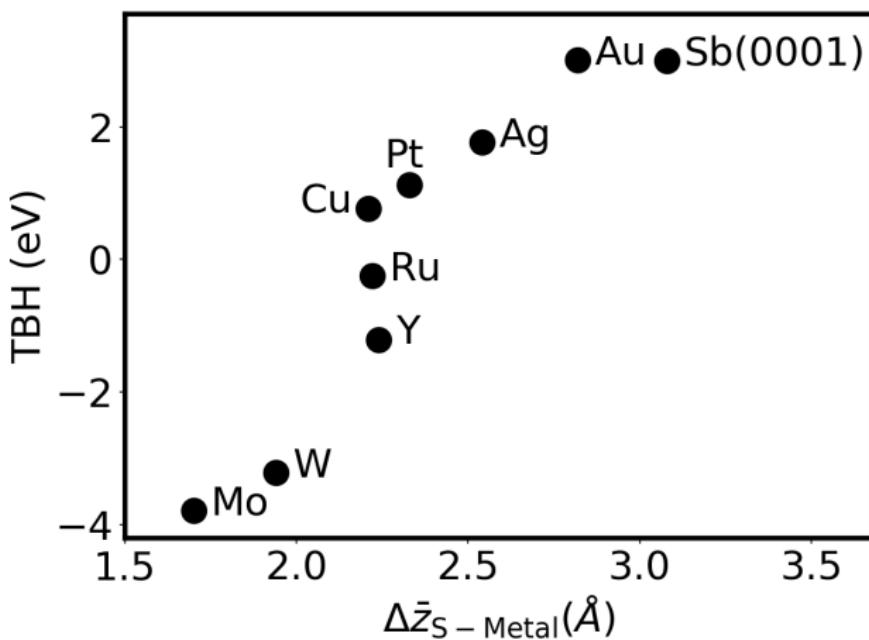
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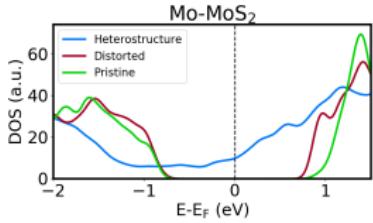
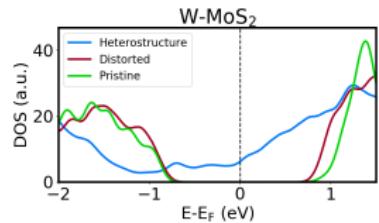
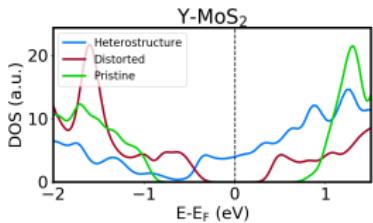
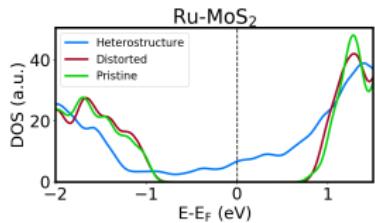
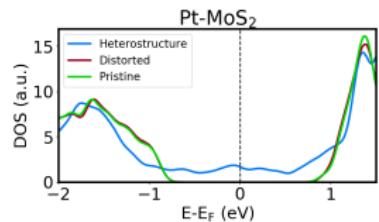
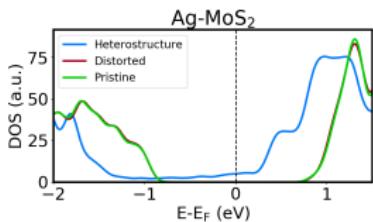
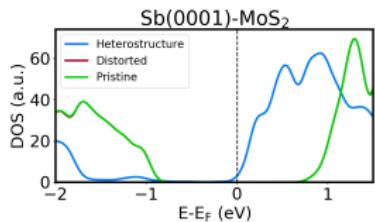
Tunneling Characteristics



Tunneling Characteristics



Density of States



Conclusions

	Dispersion	Covalent
Tunneling	:)	:-)
Gap States	:-)	:(
Inter-material distance	:(:-)
Distortion	:-)	:(

Catch-22.

- All metal-MoS₂ interfaces are expected to exhibit some contact resistance.
- Intermediate materials may be a better choice for low contact-resistance heterojunctions with MoS₂.

Introduction
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Electrides
oooooooo

Interfaces
oooooooo

Future Work
oooo

Introduction

Electrides

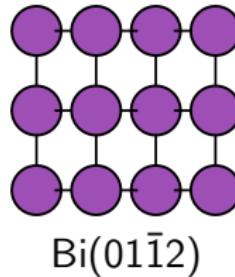
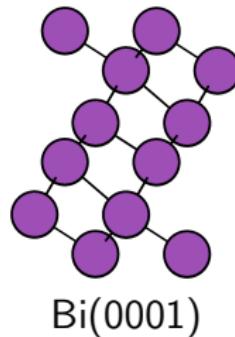
Interfaces

Future Work

Outstanding Metal-MoS₂ Interfaces

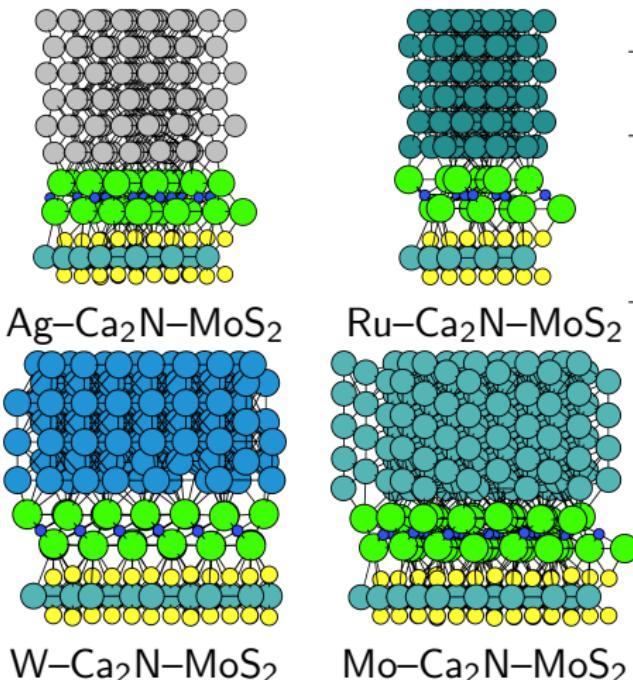
Metal	Metal–MoS ₂	$\varepsilon_{\text{metal}} (\%)$	N_{atoms}
Bi(0001)		+0.41	111
Bi(01̄12)		-3.94	172
Sb(01̄12)		-1.42	246

The (01̄12) plane of Sb has shown low contact resistance to MoS₂. These planes may be useful as points of reference.



⁵ *Nature* **613**, 274–279 (2023).

Metal- Ca_2N - MoS_2 Interfaces



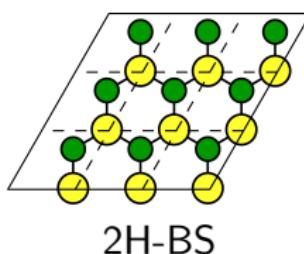
Metal	Metal- Ca_2N - MoS_2		
	$\varepsilon_{\text{metal}} (\%)$	$\varepsilon_{\text{Ca}_2\text{N}} (\%)$	N_{atoms}
Ag	+1.21	+0.04	201
Ru	-1.59	+0.04	126
W	+0.98	+1.84	182
Mo	+2.03	+1.18	301

Heterostructures are still undergoing relaxation.

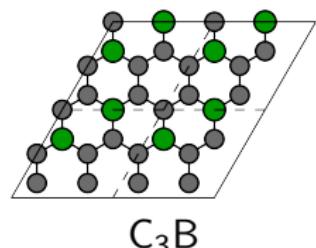
High Electron-Affinity Layered Materials

p-type contacts are critical for semiconductor devices.

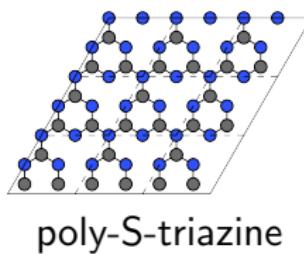
An “anti-electride” must have an electron affinity large enough to withdraw charge from a MoS_2 monolayer.



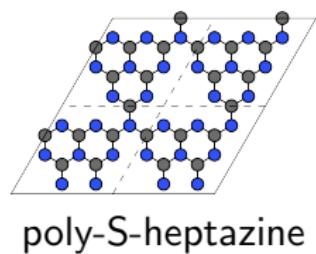
2H-BS



C_3B



poly-S-triazine



poly-S-heptazine

SUMMARY

- Importance of layered materials for device miniaturization.
- DFT+Disp. predicts electride geometries accurately compared to experiment.
- Layered electrides exhibit minimal thermal expansion.
- Metal–MoS₂ interfaces are bound by dispersion or covalent interactions which lead to a separate origins of contact resistance.
- Future work will look at Metal–Ca₂N–MoS₂ heterojunctions.