

# Rashba and Excitonic Physics in Emerging Materials and Correlations with Light-Matter Interaction: A Computational Insight

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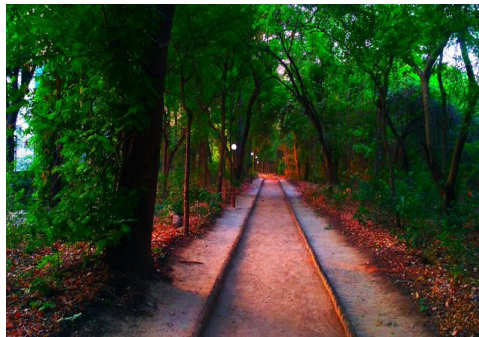
An Aided Institute of Department of Atomic Energy and A C.I. of Homi Bhabha National Institute (HBNI)

## Long Term Collaborators

 UNIVERSITY OF CAMBRIDGE Prof. David J. Wales

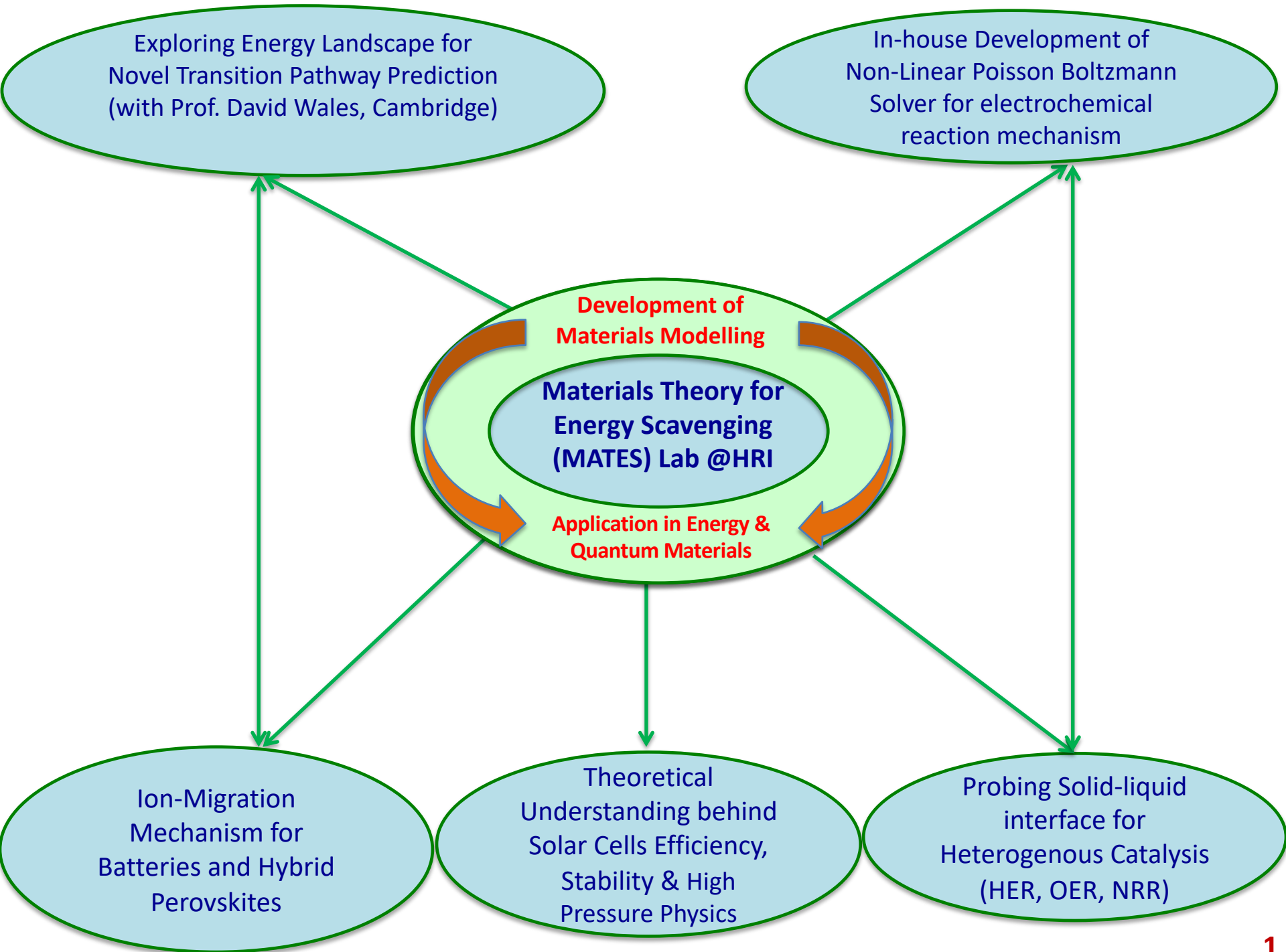
 PRINCETON UNIVERSITY Prof. Leslie Schoop

 PURDUE UNIVERSITY Prof. Babak Anasori



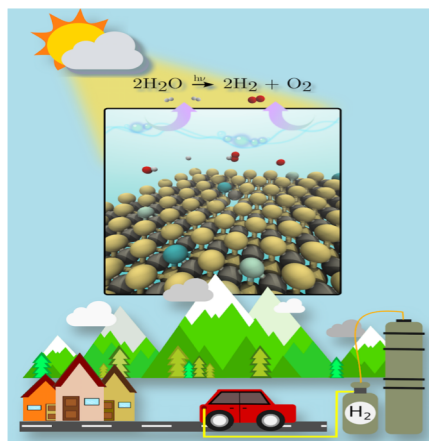
**Webpage:** <https://www.hri.res.in/~sudipchakraborty/>

FRS, IAS, Princeton



# Materials Modelling for Quantum Materials and Energy

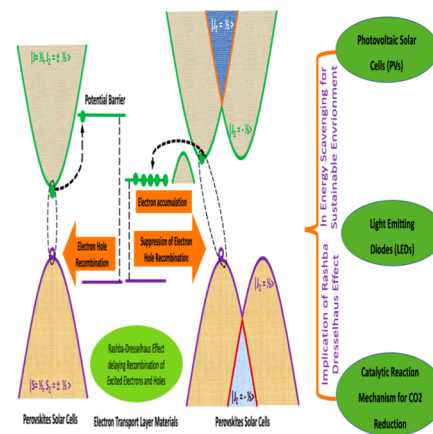
**Probing Catalytic Pathways & Dissociation Rates** → To probe Rare Events for Efficient H<sub>2</sub> production (2D Materials/Oxide surfaces)



**Structural Transformation & Diffusion Mechanism in Battery Materials** → To Engineer Crystal Structure during Charging/Discharging



**Paradigm of Rashba Phenomena and its Repercussions** → To Probe Spin Texture under Structural Compression in Emerging Perovskite Materials



ACS Energy Letters, 9, 2367 (2024)

ACS Energy Letters, 7, 3401 (2022)

Chem. Mater, in press (2026)

JACS, 145, 8634, (2023)

Advanced Materials, 34, 2202294 (2022)

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Nature Materials, 23, 960 (2024)

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ACS Nano, 18, 5684, (2024)

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Physical Review B, 112, 125107 (2025)

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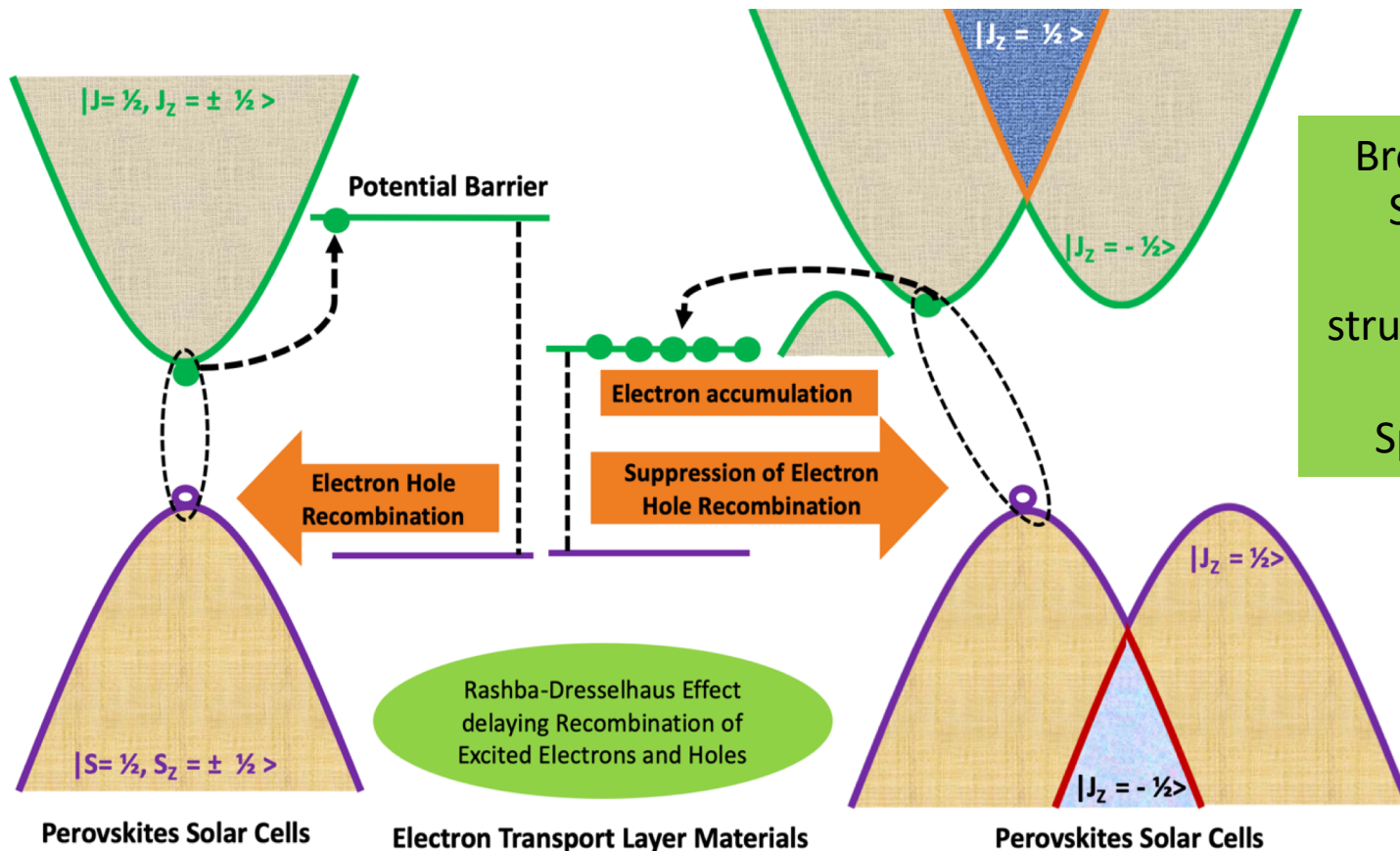
Physical Review B, 112, 214517(2025)

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Materials Today, 60, 183 (2022)



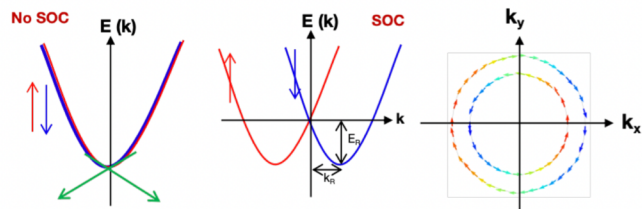
# Emerging Rashba Phenomena: Repercussion on Charge Carrier Recombination



Broken Spin-inversion Symmetry in Non-centrosymmetric structure, prevailed with Relativistic Spin-Orbit Coupling

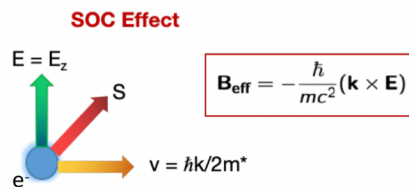
# Emerging Rashba Phenomena: Repercussion on Charge Carrier Recombination

- Time reversal symmetry:  $E(\mathbf{k}, \uparrow) = E(-\mathbf{k}, \downarrow)$
- Spatial inversion symmetry:  $E(\mathbf{k}, \uparrow) = E(-\mathbf{k}, \uparrow)$



No Rashba spin splitting  
 $E(\mathbf{k}, \uparrow) = E(-\mathbf{k}, \downarrow)$   
 $E(\mathbf{k}, \uparrow) \neq E(-\mathbf{k}, \uparrow)$

Rashba spin splitting  
 $E(\mathbf{k}, \uparrow) = E(-\mathbf{k}, \downarrow)$   
 $E(\mathbf{k}, \uparrow) \neq E(-\mathbf{k}, \uparrow)$



The **Rashba** Hamiltonian:

$$H_R = \alpha_R(\mathbf{k} \times \hat{z}) \cdot \boldsymbol{\sigma} = \alpha_R(k_y\sigma_x - k_x\sigma_y)$$

The **Dresselhaus** Hamiltonian:

$$H_D = \beta_D(k_x\sigma_x - k_y\sigma_y)$$

The **Persistent** Hamiltonian:

$$H_{\text{PST}} = \alpha_{\text{PST}}(k_x\sigma_y) \quad \text{or} \quad \alpha_{\text{PST}}(k_y\sigma_x)$$

The **3D Rashba** Hamiltonian:

$$H_R^{3D} = \frac{\alpha_0 e \hbar}{4m_0^2 c^2} [\nabla \mathbf{V} \times \mathbf{P}] \cdot \boldsymbol{\sigma} = \frac{\alpha_0 e \hbar^2}{4m_0^2 c^2} [\mathbf{k} \times \mathbf{E}] \cdot \boldsymbol{\sigma}$$

- Band splitting due to Rashba effects enhances the lifetime of charge carriers because of spin-forbidden transitions<sup>1,2</sup>.
- spin-charge conversion, creation and detection of spin currents - spintronics<sup>3</sup>.

- Rashba Hamiltonian:

$$\hat{H}_R = \frac{e\hbar}{2m}(\boldsymbol{\sigma} \cdot \mathbf{B}) = \alpha_R(\boldsymbol{\sigma} \times \mathbf{k}) \cdot \hat{z}$$

- The Hamiltonian for a 2DEG, including the Rashba term:

$$\hat{H}_R = \frac{\hbar^2 k^2}{2m} + \alpha_R(\boldsymbol{\sigma} \times \mathbf{k}) \cdot \hat{z}$$

- Corresponding eigenvalues-

$$E_{\pm} = \frac{\hbar^2 k^2}{2m} \pm \alpha_R k = \frac{\hbar^2}{2m}(k \pm k_R)^2 + E_R$$

$$\alpha_R = \frac{2E_R}{k_R}$$

- And corresponding eigenstates

$$|\psi_{\pm}(k)\rangle = \frac{1}{\sqrt{2}} \begin{pmatrix} \pm e^{-i\theta} \\ 1 \end{pmatrix}$$

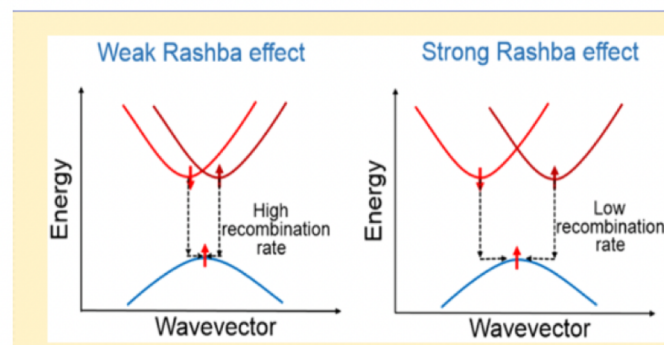
- The spin texture can be calculated from the expectation value of Pual's spin operator  $\boldsymbol{\sigma}$ , expressed as

$$\langle \psi_{\pm}(k) | \boldsymbol{\sigma} | \psi_{\pm}(k) \rangle = \pm \begin{pmatrix} \cos\theta \\ -\sin\theta \\ 0 \end{pmatrix}$$

Origin of Rashba Splitting

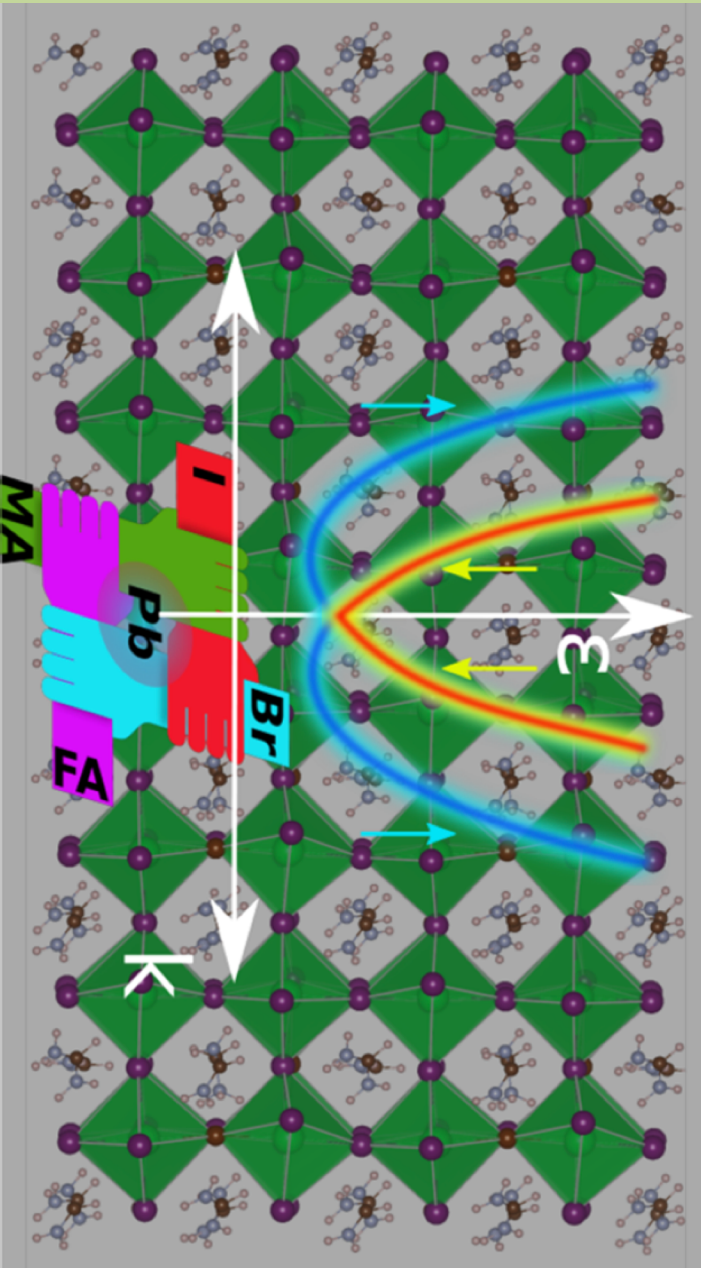
Broken Spin-inversion Symmetry in Non-centrosymmetric structure, prevailed with Relativistic Spin-Orbit Coupling

- The Rashba splitting strength influences the e-h recombination rate.



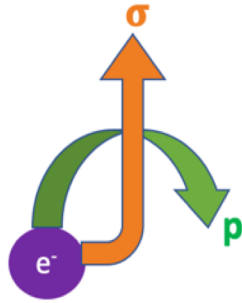
Ref. - DOI: 10.1021/acs.jpcclett.9b02936

# Emerging Rashba Phenomena: Repercussion on Charge Carrier Recombination



Multidimensional Hybrid Perovskites Family

Spin Orbit Coupling (SOC)



Inversion Symmetry Breaking

Implication of Rashba Dresselhaus Effect  
In Energy Scavenging for Sustainable Environment

Photovoltaic Solar Cells (PVs)

Light Emitting Diodes (LEDs)

Catalytic Reaction Mechanism for CO<sub>2</sub> Reduction



## Rational Design: A High-Throughput Computational Screening and Experimental Validation Methodology for Lead-Free and Emergent Hybrid Perovskites

Sudip Chakraborty,<sup>1,2,4</sup> Wei Xie,<sup>1,4</sup> Nripan Mathews,<sup>1,4</sup> Matthew Sherburne,<sup>2</sup> Rajeev Ahuja,<sup>2</sup> Mark Asta,<sup>3,5</sup> and Subodh G. Mhaisalkar<sup>1\*</sup>

## CsPbCl<sub>3</sub> → CsPbI<sub>3</sub> Exchange in Perovskite Nanocrystals Proceeds through a Jump-the-Gap Reaction Mechanism

Nikolaos Livakas, Stefano Toso,<sup>\*</sup> Yurii P. Ivanov, Tisita Das, Sudip Chakraborty, Giorgio Divitini, and Liberato Manna<sup>\*</sup>

## Colloidal Aziridinium Lead Bromide Quantum Dots

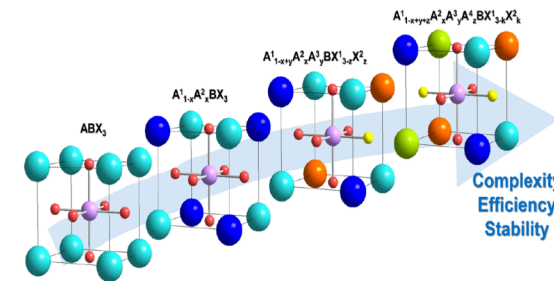
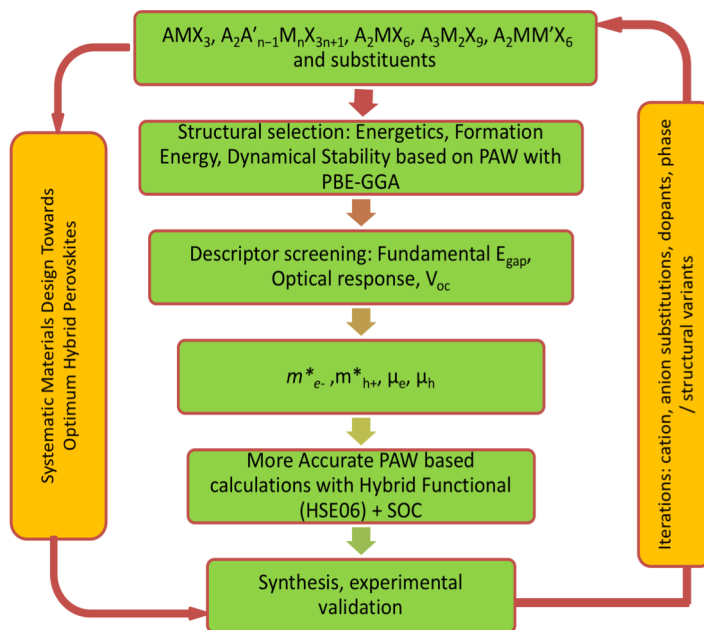
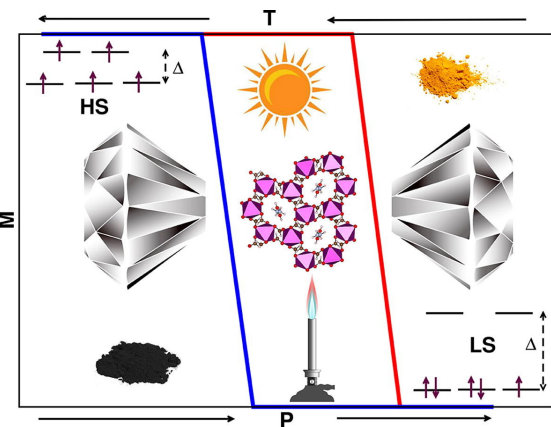
Maryna I. Bodnarchuk,<sup>\*</sup> Leon G. Feld, Chenglian Zhu, Simon C. Boehme, Federica Bertolotti, Jonathan Avaro, Marcel Aebli, Showkat Hassan Mir, Norberto Masciocchi, Rolf Erni, Sudip Chakraborty, Antonietta Guagliardi, Gabriele Rainò, and Maksym V. Kovalenko<sup>\*</sup>

Applied Physics Reviews REVIEW scitation.org/journal/apr

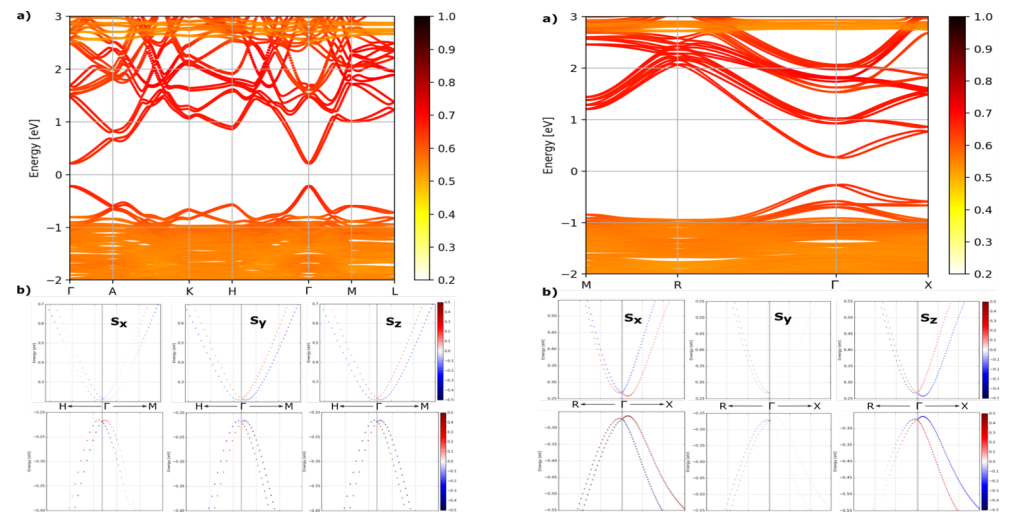
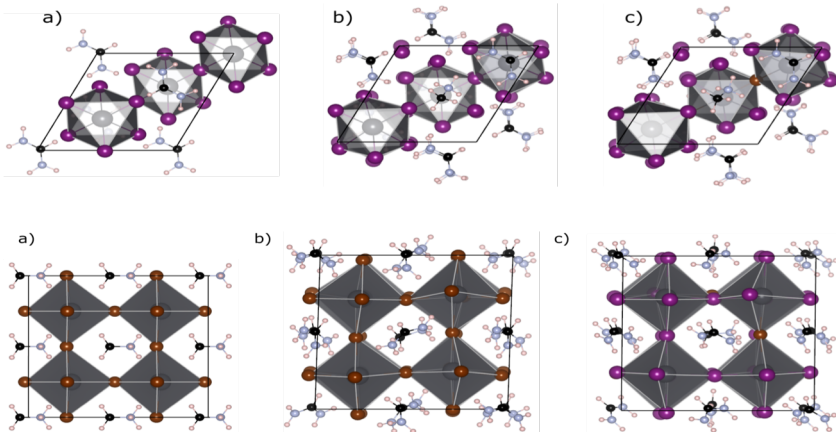
## Evolution of hybrid organic-inorganic perovskite materials under external pressure

Cite as: Appl. Phys. Rev. 8, 041309 (2021); doi:10.1063/1.50053128  
Submitted: 5 April 2021 | Accepted: 21 September 2021 |  
Published Online: 25 October 2021

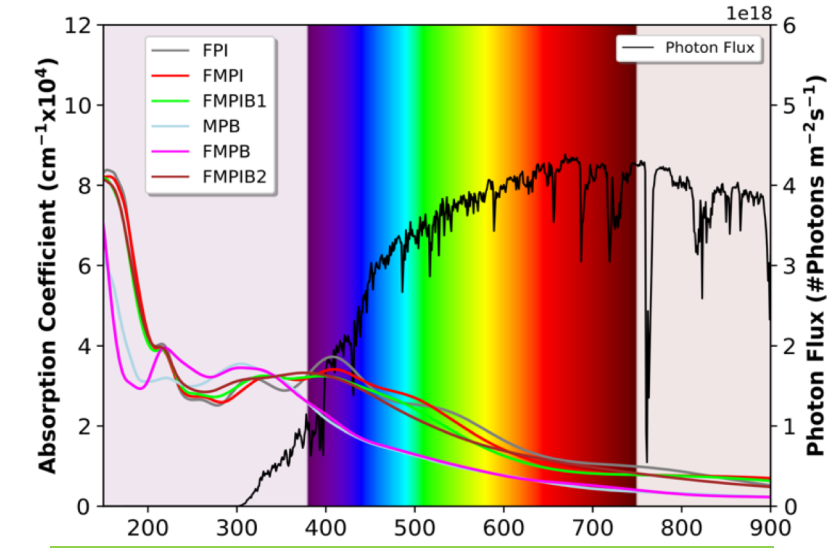
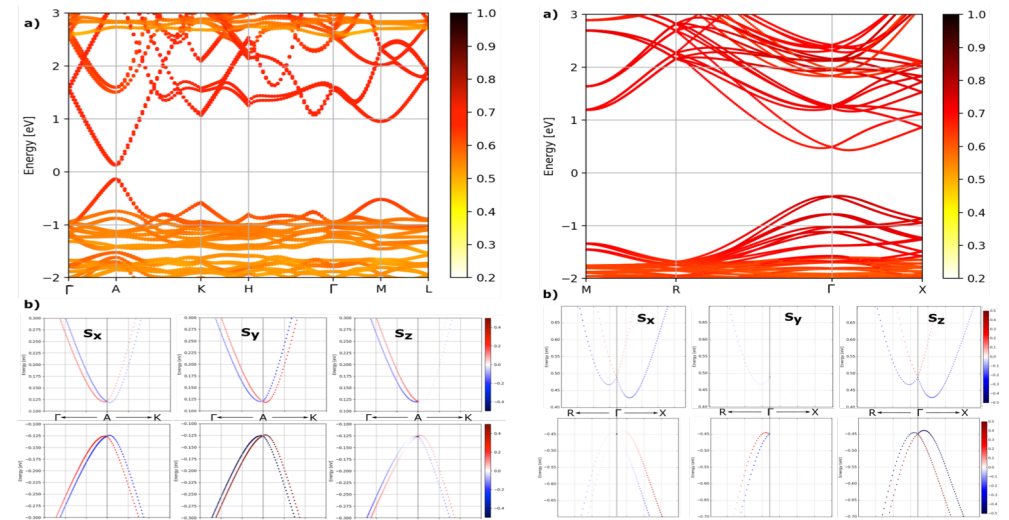
Manasa G. Basavarajappa,<sup>1</sup> Mohammad Khaja Nazeeruddin,<sup>1,2</sup> and Sudip Chakraborty<sup>1,3</sup>



# Unveiling Rashba Phenomena in Hybrid Halide Perovskite



Crystal structure of (a) FPI, (b) FMPI, (c) FMPIB1, (d) MPB (e) FMPB (f) FMPIB2. Violet, brown, black, pink, and sky-blue ball represents I, Br, C, H, N atoms respectively. Gray polyhedral represent Pb-polyhedra.



Band structure of (a) FMPIB1, (b) FMPIB2, (c) FPI, (d) MPB. The projection of three spin component ( $S_x$ ,  $S_y$ ,  $S_z$ ) near CBM and VBM at the high symmetry point,  $\Gamma$  are represented for (c) FMPIB1, (d) FMPIB2, (e) FPI and (f) MPB. Red and blue represents respectively projection of spin-up and spin-down states as shown by color scale.

Optical Response of mixed cation-mixed halide Hybrid Perovskites

# Connecting Rashba Physics with Pressure Driven Tuning of Structural, Electronic and Optical Properties: *Piezochromism*

# Connecting Rashba Physics with Pressure Driven Tuning of Structural, Electronic and Optical Properties: *Piezochromism*

## High pressure-induced distortion in face-centered cubic phase of thallium

Komsilp Kotmool<sup>a,b</sup>, Bing Li<sup>c,d,e</sup>, Sudip Chakraborty<sup>f</sup>, Thiti Bovornratanaraks<sup>b,g</sup>, Wei Luo<sup>f</sup>, Ho-kwang Mao<sup>c,d,h,i</sup>, and Rajeev Ahuja<sup>k,l</sup>

<sup>a</sup>Department of Physics, Mahidol Wittayanusorn School, Nakhon Pathom 73170, Thailand; <sup>b</sup>Thailand Center of Excellence in Physics, Commission on Higher Education, Bangkok 10400, Thailand; <sup>c</sup>High Pressure Synergetic Consortium, Carnegie Institution of Washington, Argonne, IL 60439; <sup>d</sup>Center for High Pressure Science and Technology Advanced Research, Shanghai 201203, China; <sup>e</sup>Center for the Study of Matter at Extreme Conditions, Department of Mechanical and Materials Engineering, Florida International University, Miami, FL 33199; <sup>f</sup>Condensed Matter Theory Group, Department of Physics and Astronomy, Uppsala University, S-75120 Uppsala, Sweden; <sup>g</sup>Extreme Conditions Physics Research Laboratory, Department of Physics, Faculty of Science, Chulalongkorn University, Bangkok 10330, Thailand; <sup>h</sup>Geophysical Laboratory, Carnegie Institution of Washington, Washington, DC 20015; and <sup>i</sup>Applied Materials Physics, Department of Materials and Engineering, Royal Institute of Technology, S-100 44 Stockholm, Sweden

## Systematic Tuning of Structural/Electronic/Optical Properties

## Revealing an unusual transparent phase of superhard iron tetraboride under high pressure

Komsilp Kotmool<sup>a</sup>, Thanayut Kaewmaraya<sup>b</sup>, Sudip Chakraborty<sup>b</sup>, Jonas Anversa<sup>c</sup>, Thiti Bovornratanaraks<sup>a,d</sup>, Wei Luo<sup>b</sup>, Huiyang Gou<sup>e</sup>, Paulo Cesar Piquini<sup>f</sup>, Tae Won Kang<sup>f</sup>, Ho-kwang Mao<sup>g,h,i</sup>, and Rajeev Ahuja<sup>k,l,m</sup>

<sup>a</sup>Center of Excellence in Forum for Theoretical Science, Department of Physics, Faculty of Science, Chulalongkorn University, Bangkok 10330, Thailand; <sup>b</sup>Condensed Matter Theory Group, Department of Physics and Astronomy, Uppsala University, S-75120 Uppsala, Sweden; <sup>c</sup>Departamento de Física, Universidade Federal de Santa Maria, 97105-900 Santa Maria, Rio Grande do Sul, Brazil; <sup>d</sup>Thailand Center of Excellence in Physics, Commission on Higher Education, Bangkok 10400, Thailand; <sup>e</sup>Geophysical Laboratory, Carnegie Institution for Science, Washington, DC 20015; <sup>f</sup>Quantum Functional Semiconductor Research Center, Dongguk University, Chung gu, Seoul 100-715, Korea; <sup>g</sup>Center for High Pressure Science and Technology Advanced Research, Shanghai 201203, People's Republic of China; and <sup>h</sup>Applied Materials Physics, Department of Materials and Engineering, Royal Institute of Technology, S-100 44 Stockholm, Sweden

Composition Change in the Structural Unit

Functionalization with Foreign Elements

External Stimuli like Temperature

Lattice Compression/Hydrostatic Pressure

Excited State Dynamics

Thermodynamic Distribution of Lattice Defects

Finite Shift of Optical Response Peak/ Band Gap Tuning

Access new structure, not possible through conventional syntheses

Hybrid Perovskites with Soft Lattices exhibits LARGE Pressure Response

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Communication  
pubs.acs.org/JACS

Pressure-Induced Metallization of the Halide Perovskite  $(\text{CH}_3\text{NH}_3)\text{PbI}_3$

Adam Jaffe,<sup>1</sup> Yu Lin,<sup>1,2</sup> Wendy L. Mao,<sup>1,3</sup> and Hemamala I. Karunadasa<sup>1,4</sup>

<sup>1</sup>Departments of <sup>2</sup>Chemistry and <sup>3</sup>Geological Sciences, Stanford University, Stanford, California 94305, United States

<sup>4</sup>Photon Science and Stanford Institute for Materials and Energy Sciences, SLAC National Accelerator Laboratory, Menlo Park, California 94025, United States

# Pressure Driven Rashba Splitting in Inorganic Nitride Perovskite $\text{CeTaN}_3$

## $\text{CeTaN}_3$ and $\text{CeNbN}_3$ : Prospective Nitride Perovskites with Optimal Photovoltaic Band Gaps

Viet-Anh Ha, Hyungjun Lee, and Feliciano Giustino\*

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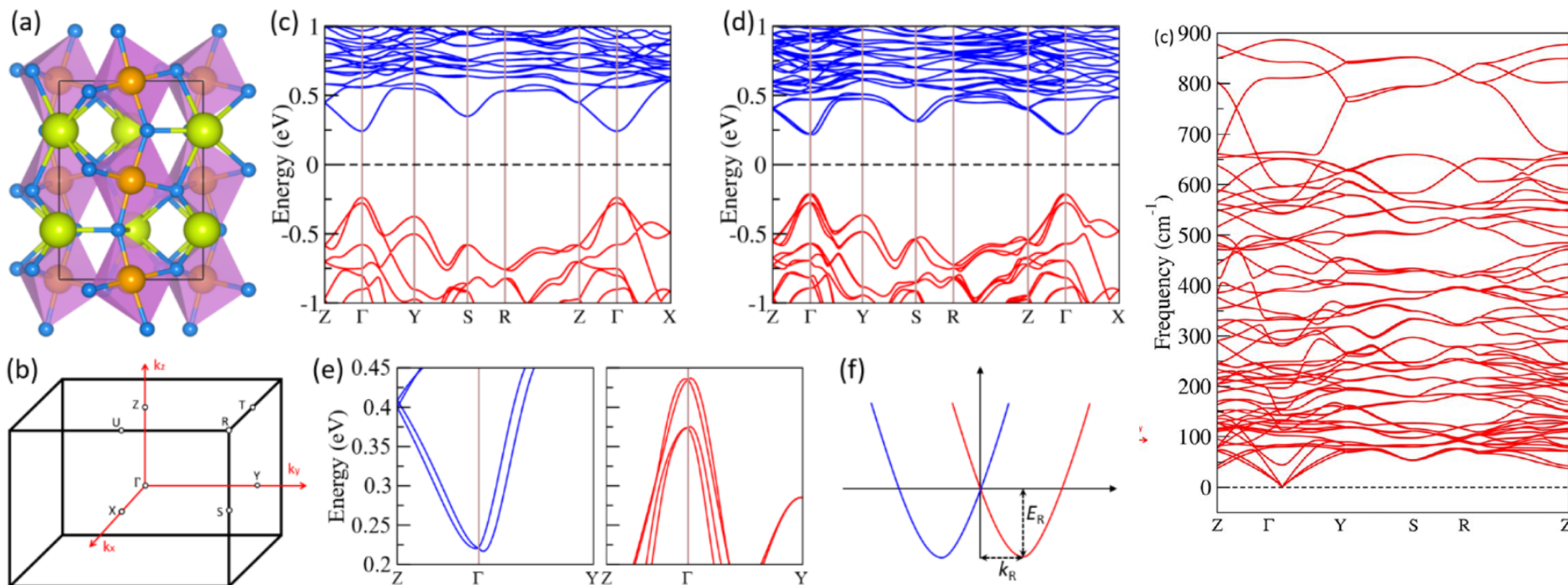
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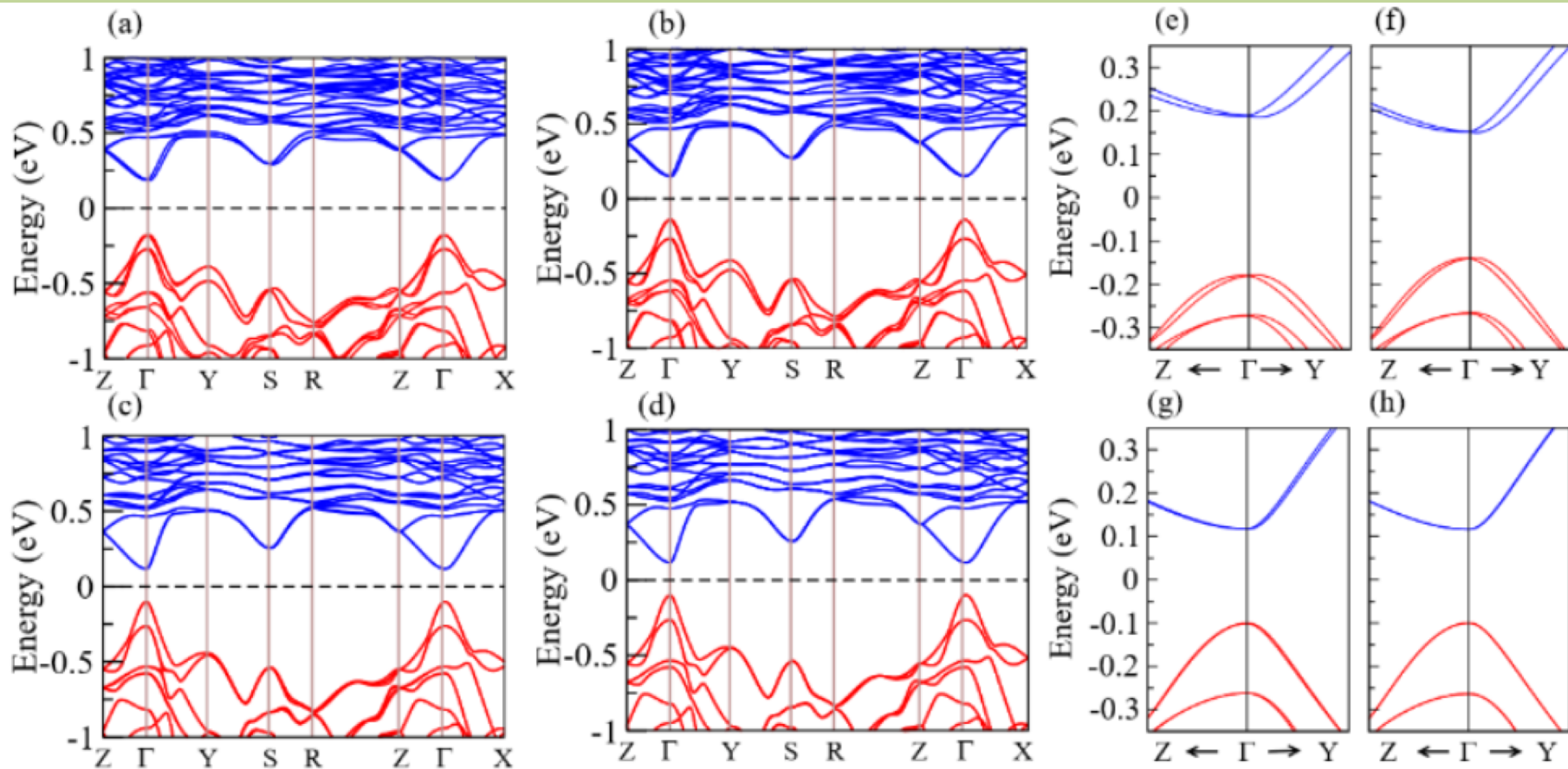
## Spin texture evolution of Rashba splitting under pressure: a case study of inorganic nitride perovskite crystals†

Showkat H. Mir<sup>ab</sup> and Sudip Chakraborty<sup>ca\*</sup>



(a)  $\text{CeTaN}_3$  orthorhombic phase with distortions ( $Pmn21$ ); (b) First Brillouin zone of orthorhombic cell displaying high symmetry  $k$ -points; Band structure (c) without SOC and (d) with SOC; (e) Zoom-in view of band edges: Conduction band (left) and valence band (right), (f) Schematic showing Rashba Splitting ( $E_R$ ) and momentum offset ( $k_R$ ).

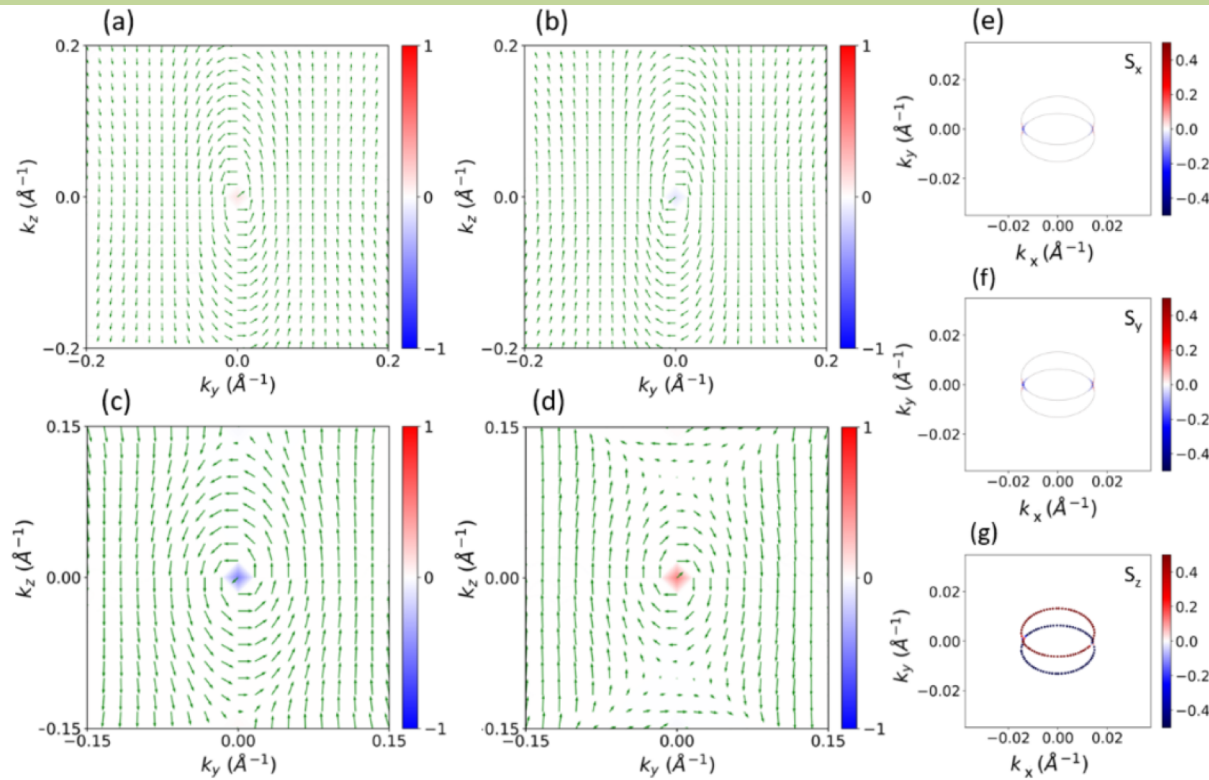
# Pressure Driven Rashba Splitting in Inorganic Nitride Perovskite $\text{CeTaN}_3$



Pressure evolution of band structure and Rashba splitting of  $\text{CeTaN}_3$ : (a, e) 2 GPa; (b, f) 4 GPa; (c, g) 6 GPa; (d, h) 8 GPa.

- Rashba splitting decreases with pressure in (e-f) (zoomed-in view)
- Spin splitting of valence and conduction bands disappears at 6 GPa and 8 GPa, respectively.

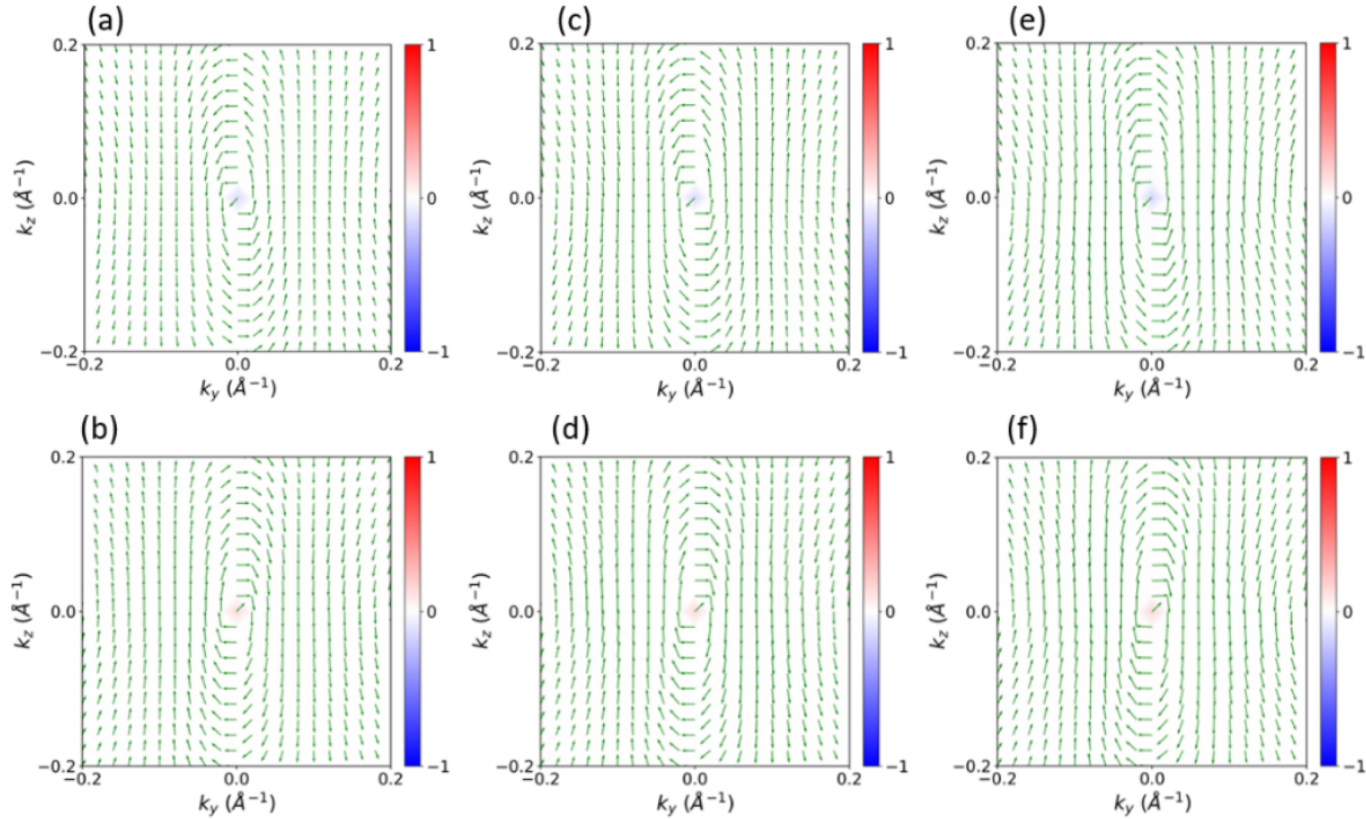
# Pressure Driven Rashba Splitting in Inorganic Nitride Perovskite $\text{CeTaN}_3$



*Spin textures of  $\text{CeTaN}_3$  around  $\Gamma$  point*

- Spin configuration at CBM (a, b) & VBM (c, d), left panel (outer), middle panel (inner branch) in  $k_y$ - $k_z$  plane.
- The green arrows show the in-plane component, and colour bar designates the out-of-plane spin component.
- Constant energy contours in (e)–(g) show  $S_x$ ,  $S_y$  and  $S_z$  spin components in conduction band at 0.25 eV.
- The colour scale in panels (e)–(g) shows up and down spin components.

# Pressure Driven Rashba Splitting in Inorganic Nitride Perovskite $\text{CeTaN}_3$



*Spin textures of  $\text{CeTaN}_3$  around  $\Gamma$  point*

Pressure	<b>a</b>	<b>b</b>	<b>c</b>	$\Delta E_{for}$	$E_g$	$\alpha(\text{CB})$	$\alpha(\text{VB})$		
0	5.613	5.729	7.962	-6.555	0.436	0.399	0.079	0.282	0.154
2	5.596	5.709	7.943	-6.552	0.364	0.418	0.078	0.294	0.144
4	5.580	5.690	7.924	-6.538	0.290	0.406	0.065	0.300	0.124
6	5.563	5.670	7.904	-6.517	0.218	0.062	0.012	0.047	0
8	5.550	5.654	7.883	-6.492	0.216	0	0	0	0

# Pressure Induced Rashba Evolution in 1D-Halide Perovskites (3AMP)BiI<sub>5</sub>

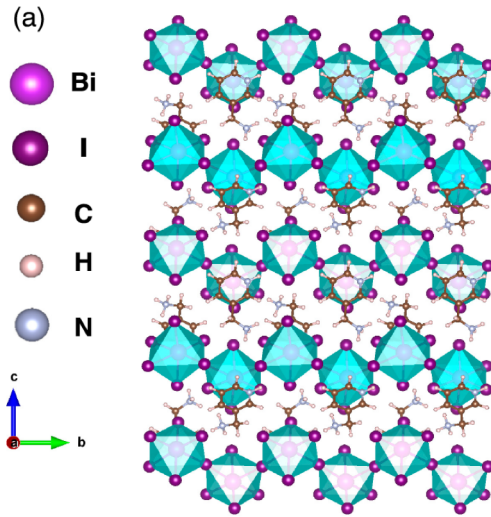
PHYSICAL REVIEW MATERIALS 8, 055405 (2024)

## Unraveling Rashba effect through spin-texture evolution in unidimensional-confined halide-perovskite under compression

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Materials Theory for Energy Scavenging Lab, Harish-Chandra Research Institute, A CI of Homi Bhabha National Institute, Chhatnag Road, Jhansi, Prayagraj 211019, India

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Pressure (GPa)	Rashba energy $E_R$ (meV)		Momentum offset $k_0$ ( $10^{-3} \text{ \AA}^{-1}$ )		Rashba splitting $\alpha_R$ (eVÅ)	
	$\Gamma \rightarrow A$	$\Gamma \rightarrow B$	$\Gamma \rightarrow A$	$\Gamma \rightarrow B$	$\Gamma \rightarrow A$	$\Gamma \rightarrow B$
0	0.6	0.4	25.04	9.20	0.05	0.09
1.4	7.0	0.8	106.2	14.2	0.13	0.11
2.5	19.9	0.8	127.0	14.6	0.31	0.11
3.2	18.8	0.8	119.5	14.7	0.31	0.11
6.6	13.0	1.7	96.0	20.3	0.27	0.17
9.6	3.1	1.1	39.3	20.7	0.16	0.11

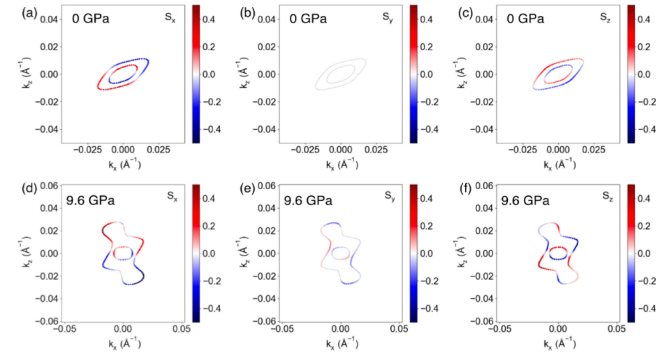


FIG. 6. Evolution of spin texture with structural compression. (a)–(c) The spin texture at ambient pressure along the  $S_x$ ,  $S_y$ , and  $S_z$  directions, respectively. The spin textures are calculated at constant energy  $E = E_F - 0.298$  eV. (d)–(f) The spin texture at 9.6 GPa along the  $S_x$ ,  $S_y$ , and  $S_z$  directions, respectively. The spin textures are calculated at constant energy  $E = E_F - 0.337$  eV.

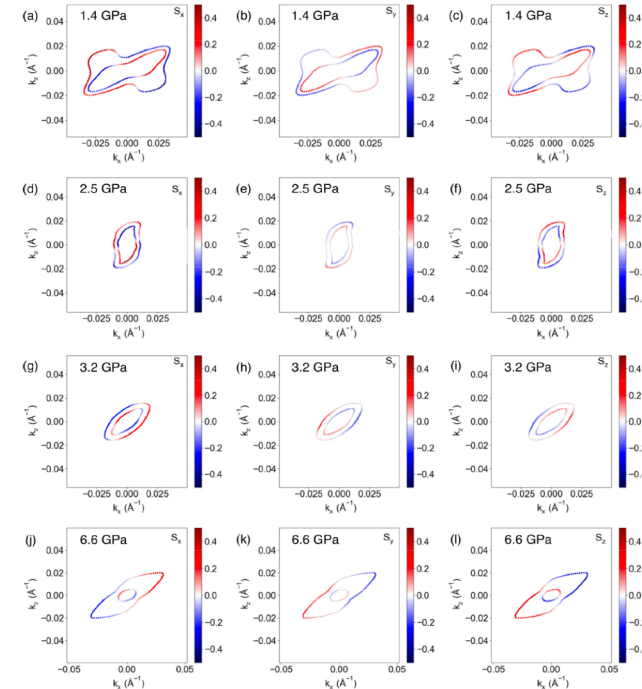


FIG. 7. Evolution of spin texture with structural compression. The first, second, and third columns denote the  $S_x$ ,  $S_y$ , and  $S_z$  directions, respectively. (a)–(c) Spin texture at 1.4 GPa and constant energy  $E = E_F - 0.315$  eV. (d)–(f) Spin texture at 2.5 GPa and constant energy  $E = E_F - 0.325$  eV. (g)–(i) Spin texture at 3.2 GPa and constant energy  $E = E_F - 0.488$  eV. (j)–(l) Spin texture at 6.6 GPa and constant energy  $E = E_F - 0.310$  eV.

# Crossover between Rashba $\rightarrow$ Rashba-Dresselhaus $\rightarrow$ Persistent Spin Texture (PST) in Quasi-2D Hybrid Perovskites

Journal of  
Materials Chemistry A

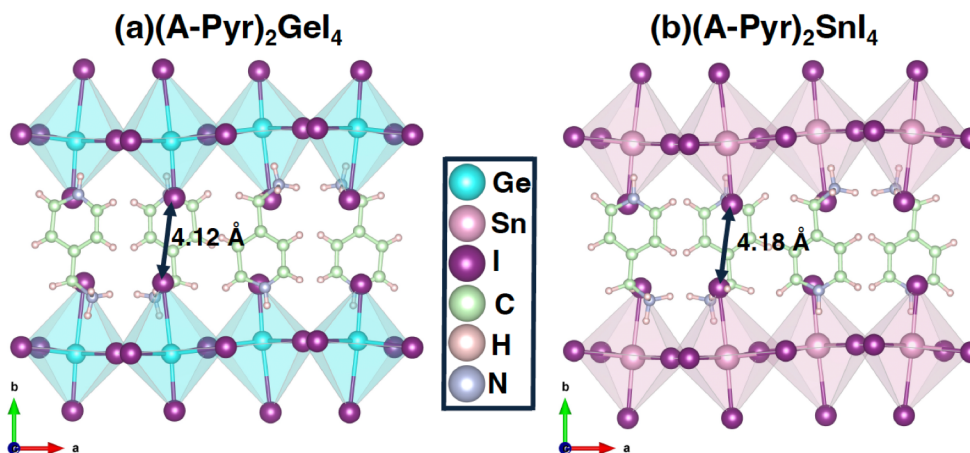
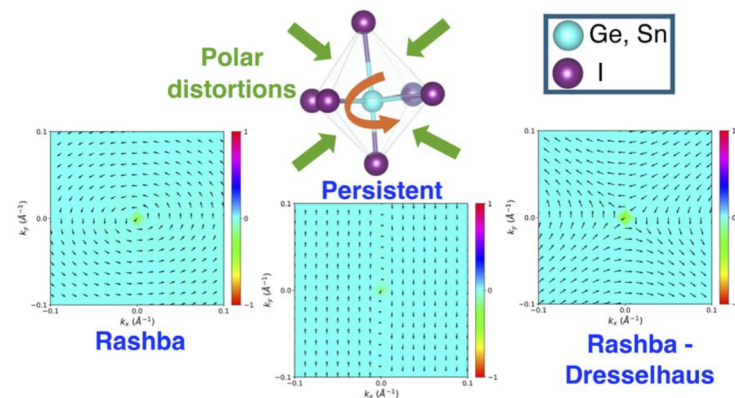


PAPER

Pressure driven interplay of Rashba, Rashba–Dresselhaus and persistent spin texture in lead-free quasi-2D hybrid perovskites

Jagjit Kaur and Sudip Chakraborty \*

Cite this: DOI: 10.1039/d5ta10066f

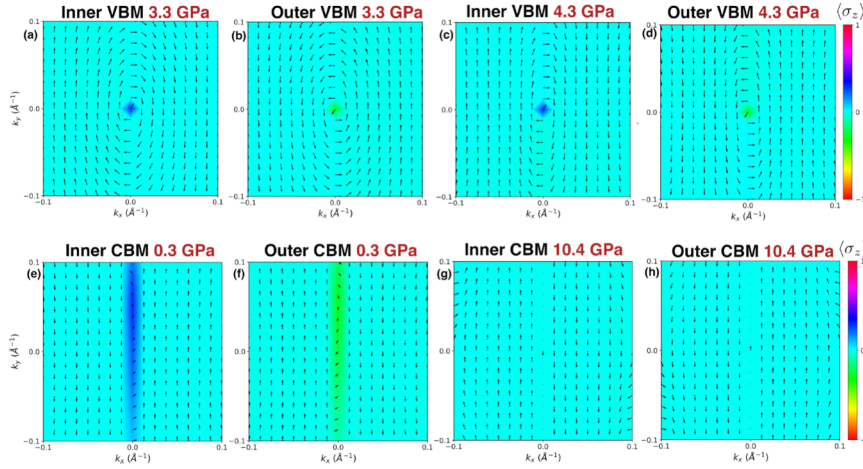


- Quasi 2D - Orthorhombic (space group  $Pca2_1$ )
- Lattice parameter:  $(A\text{-Pyr})_2\text{GeI}_4$   $a = 17.67 \text{ \AA}$ ,  $b = 10.24 \text{ \AA}$ ,  $c = 8.14 \text{ \AA}$ .  
 $(A\text{-Pyr})_2\text{SnI}_4$   $a = 18.16 \text{ \AA}$ ,  $b = 10.51 \text{ \AA}$ ,  $c = 8.16 \text{ \AA}$ .
- Bond length: Ge-I =  $3.09 \text{ \AA}$ , Sn-I =  $3.18 \text{ \AA}$

# Crossover between Rashba $\rightarrow$ Rashba-Dresselhaus $\rightarrow$ Persistent Spin Texture (PST) in Quasi-2D Hybrid Perovskites

## Spin texture in $(A\text{-Pyr})_2\text{GeI}_4$

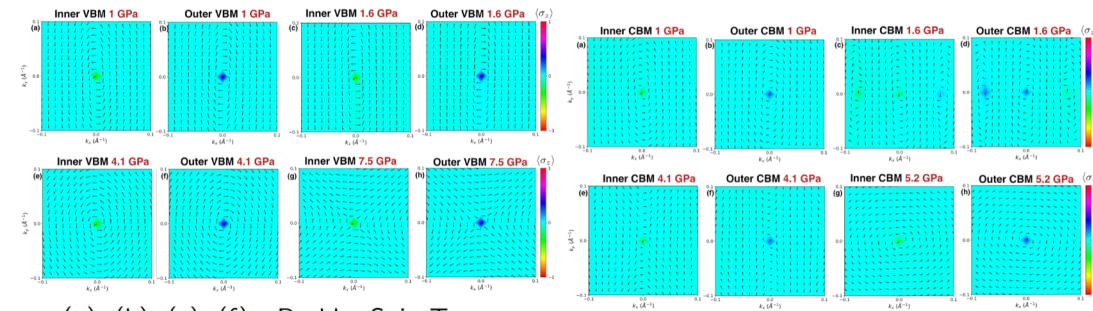
The **bond angle variance** is defined by:  $\sigma^2 = \frac{1}{m-1} \sum_{i=1}^m (\phi_i - \phi_0)^2$ ,  
 $m$  - number of faces in the polyhedron;  $\phi_i$  - the  $i$ th bond angle;  $\phi_0$  - ideal bond angle for a regular polyhedron



(a) - (b) - Rashba Spin Texture; (c) - (h) - PST

Pressure (GPa)	$\sigma^2$ ( $^\circ^2$ )	$\alpha$ (eVÅ)		Type	
		$Y \rightarrow S$	$Y \rightarrow S$	VBM	CBM
0	27.1	0.31	-	R	-
0.3	14.8	0.003	0.18	R	PST
0.6	12.5	0.1	0.12	R	PST
0.8	9.8	0.057	-	R	-
1.2	8.5	0.003	-	R	-
1.5	7.4	0.026	0.06	R	PST
2.4	7.4	0.026	0.23	R	PST
3.3	9.1	0.14	0.51	R	PST
4.3	11.9	0.18	0.61	PST	PST
5.5	16.9	0.089	0.56	PST	PST
6.9	19.6	0.15	0.5	PST	PST
8.5	25.5	0.24	0.56	PST	PST
10.4	27.7	0.44	0.73	PST	PST

## Spin texture in $(A\text{-Pyr})_2\text{SnI}_4$



(a), (b), (e), (f) - Rashba Spin Texture,  
 (c), (d) - PST,  
 (g), (h) - RD Spin texture

(a), (b), (g), (h) - Rashba Spin Texture  
 (c) - (f) - PST

Pressure (GPa)	$\sigma^2$ ( $^\circ^2$ )	$\alpha_{\text{VBM}}$ (eVÅ)		$\alpha_{\text{CBM}}$ (eVÅ)		Type	
		$Y \rightarrow S$	$Y \rightarrow \Gamma$	$Y \rightarrow S$	$Y \rightarrow \Gamma$	VBM	CBM
0	25.5	0.34	-	-	-	R	-
0.4	20.9	0.42	-	0.12	0.029	R	R
0.7	13.9	0.29	-	0.12	0.029	R	R
1.0	15.7	0.32	-	0.13	0.036	R	R
1.6	10.8	0.23	-	0.077	-	PST	PST
2.4	9.8	0.006	-	0.025	-	PST	PST
3.2	13.2	0.18	-	0.22	0.065	PST	PST
4.1	20.9	0.38	0.08	0.21	0.03	R	PST
5.2	34.0	0.4	0.24	0.14	-	R	R
6.4	61.2	0.4	0.23	0.12	0.026	R	R
7.5	150.2	0.13	0.18	0.03	0.07	RD	R

# Strain Induced Rashba Assisted Proton Reduction Tuning

*Establishing Correlation between Rashba Splitting & Proton Reduction (Repercussion of Rashba on Hydrogen Evolution Reaction - HER)*

*A New Era is knocking....*

Journal of  
Materials Chemistry A



PAPER



Cite this: DOI: 10.1039/d3ta07896e

## Establishing the correlation between Rashba spin splitting and HER activity enhancement in Janus structures<sup>†</sup>

Dhirendra Kumar<sup>†</sup> and Sudip Chakraborty<sup>†\*</sup>

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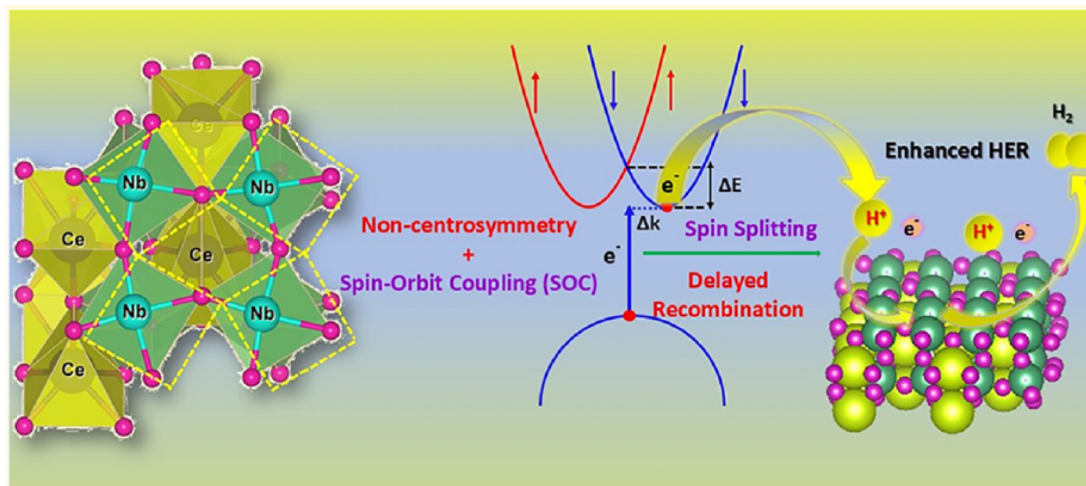
Article

## Tuning Catalytic Activity in Nitride Perovskite through Strain-Induced Rashba Spin Splitting Manipulation

Prajna Parimita Mohanty, Showkat H. Mir, Rajeev Ahuja,<sup>\*</sup> and Sudip Chakraborty<sup>\*</sup>

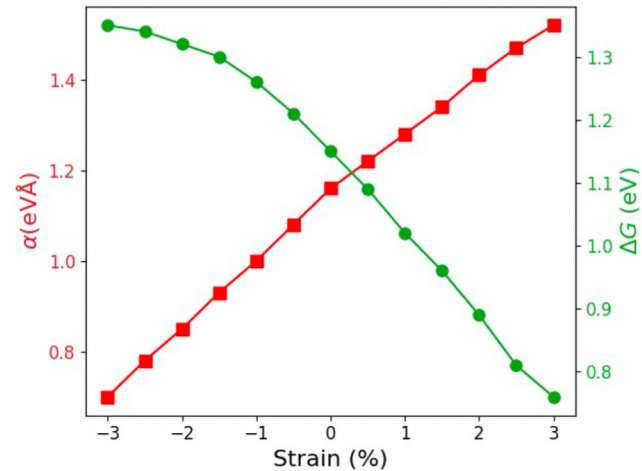
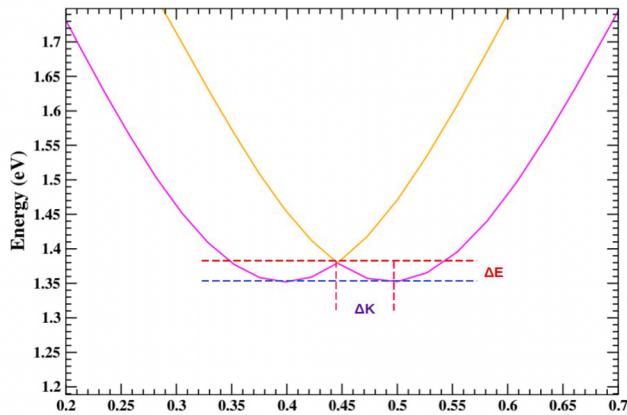
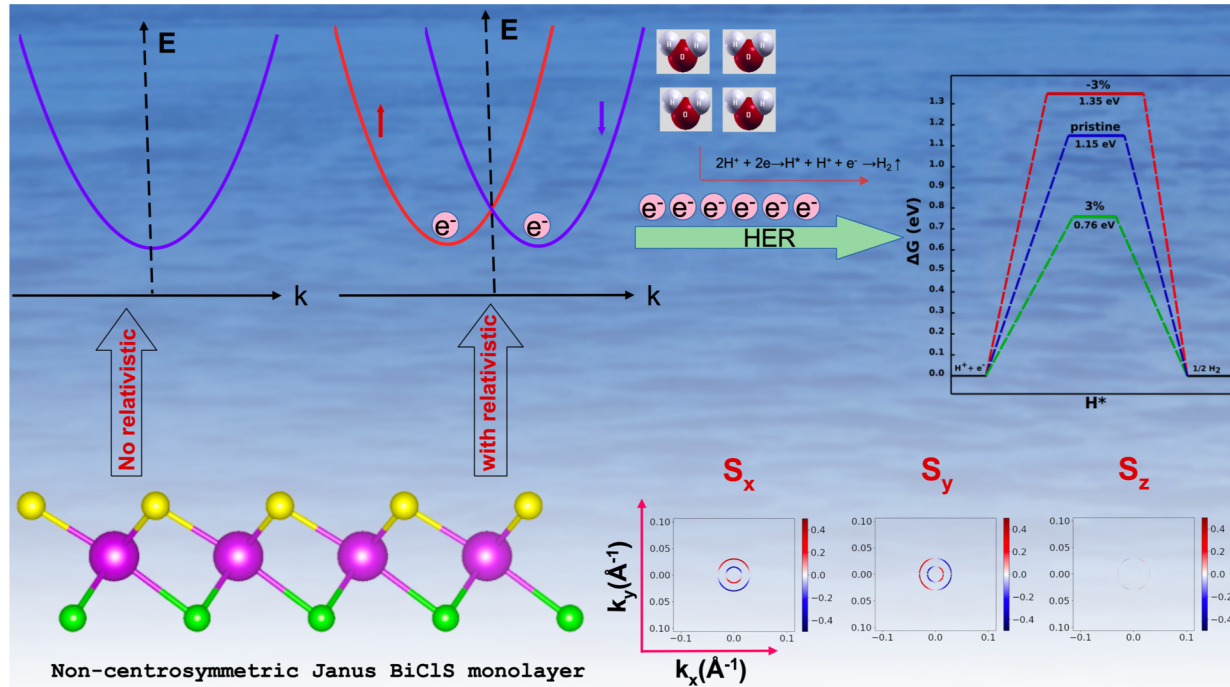
Cite This: <https://doi.org/10.1021/acs.chemmater.5c02220>

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# Implication of Rashba Phenomena in 2D Materials

## Strain Induced Rashba Assisted Proton Reduction Tuning: BiClS Janus Monolayer



# Implication of Rashba Phenomena in 2D Materials

## Strain Induced Rashba Assisted Proton Reduction Tuning: BiClS Janus Monolayer

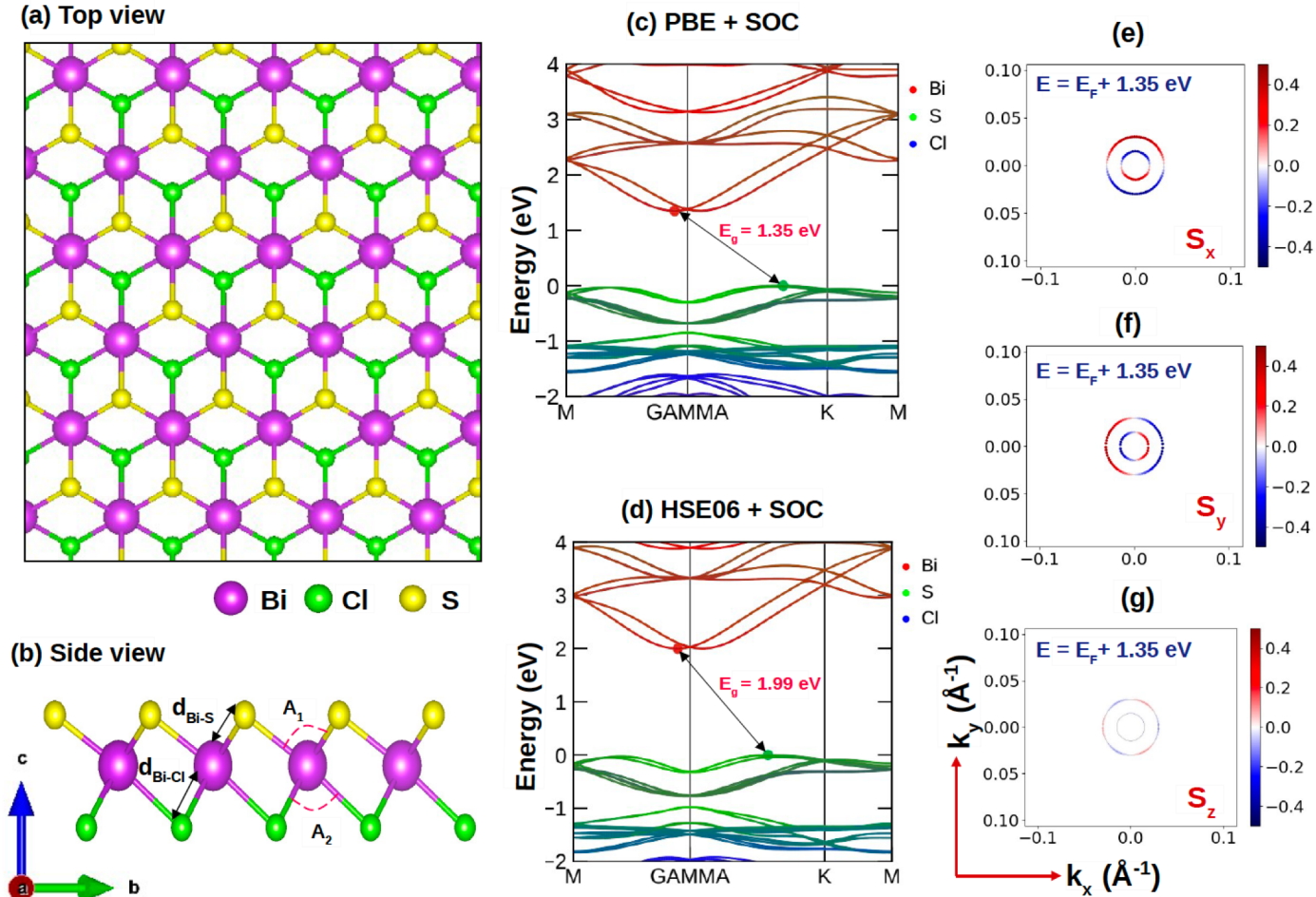


FIG. 1. (a) Top and (b) Side view of relaxed crystal structure of Janus BiClS monolayer; (c) and (d) represent the band structure considering SOC and hybrid exchange-correlation functional. The pictures (e), (f), and (g) show the spin-texture at conduction band minimum along  $S_x$ ,  $S_y$ , and  $S_z$  projections, respectively.

# Implication of Rashba Phenomena in 2D Materials

## Strain Induced Rashba Assisted Proton Reduction Tuning: BiClS Janus Monolayer

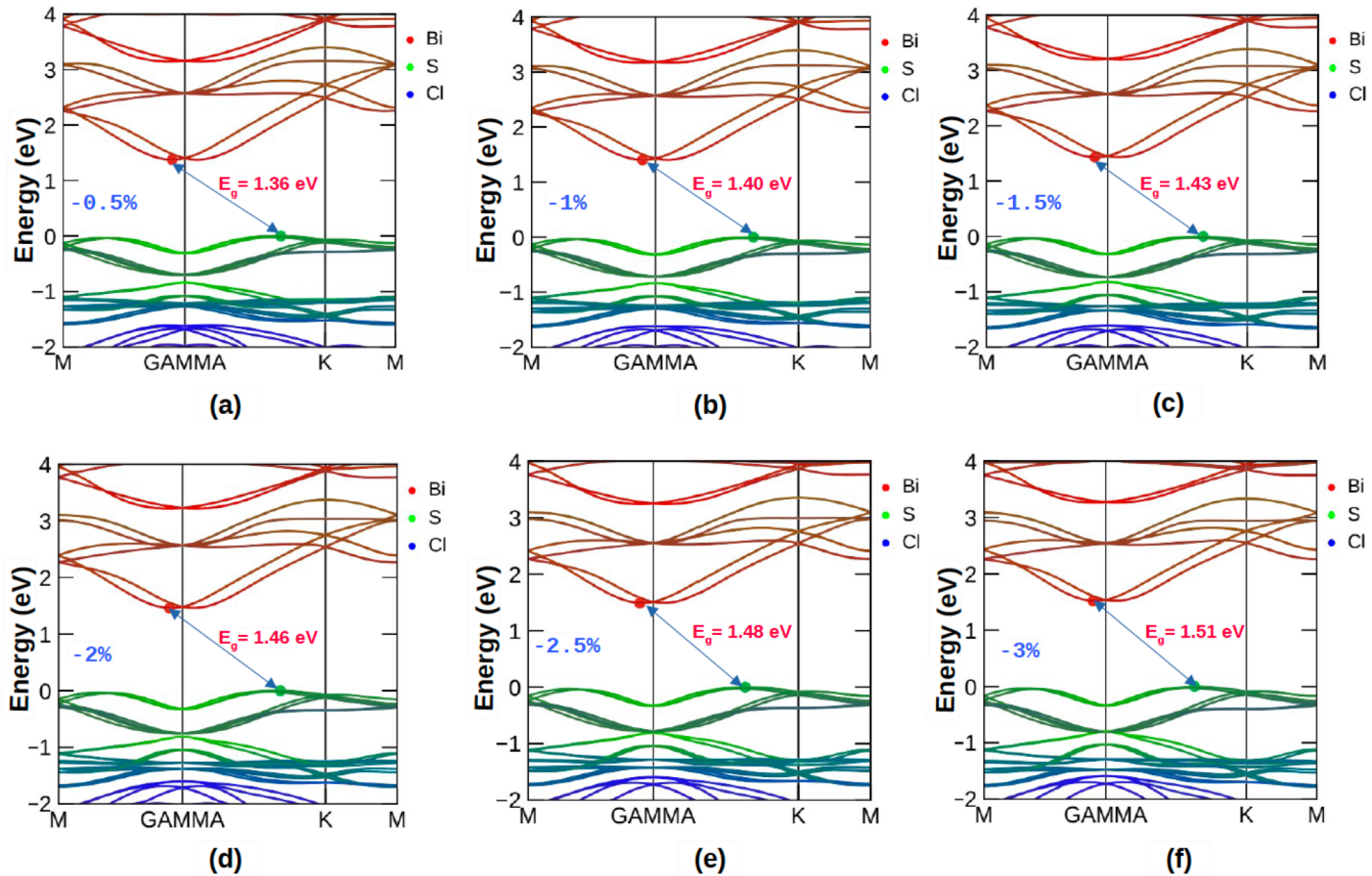


FIG. 2. Band structures of compressive strained BiClS monolayer obtained using PBE+SOC. Fig. (a) to (f) show the band structures of monolayer under the compressive strain from 0.5% to 3%. The valence band maxima is set to zero. The values with red (blue) color in all plots represent the bandgap and percentage of applied biaxial strain.

# Implication of Rashba Phenomena in 2D Materials

## Strain Induced Rashba Assisted Proton Reduction Tuning: BiClS Janus Monolayer

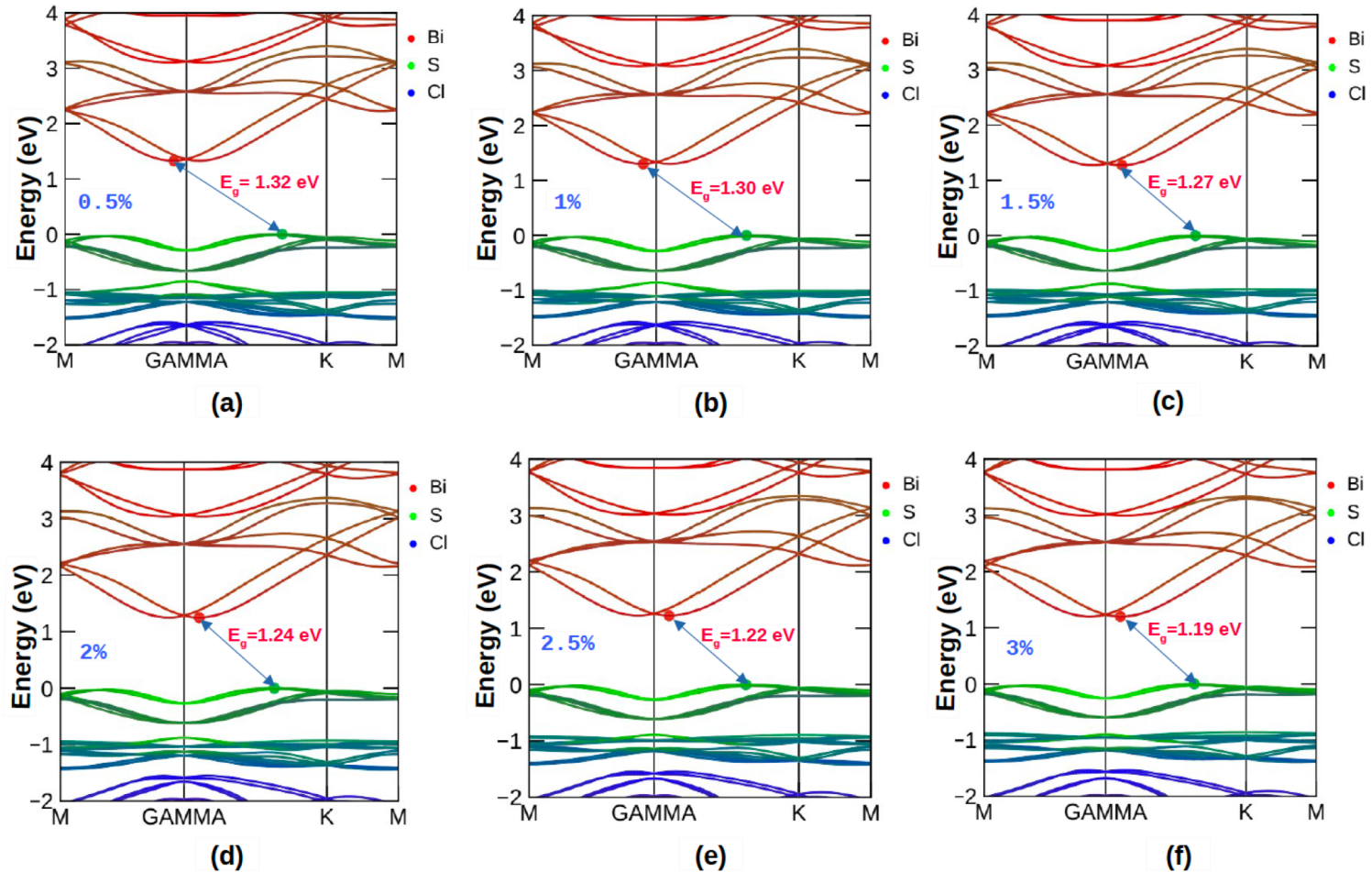
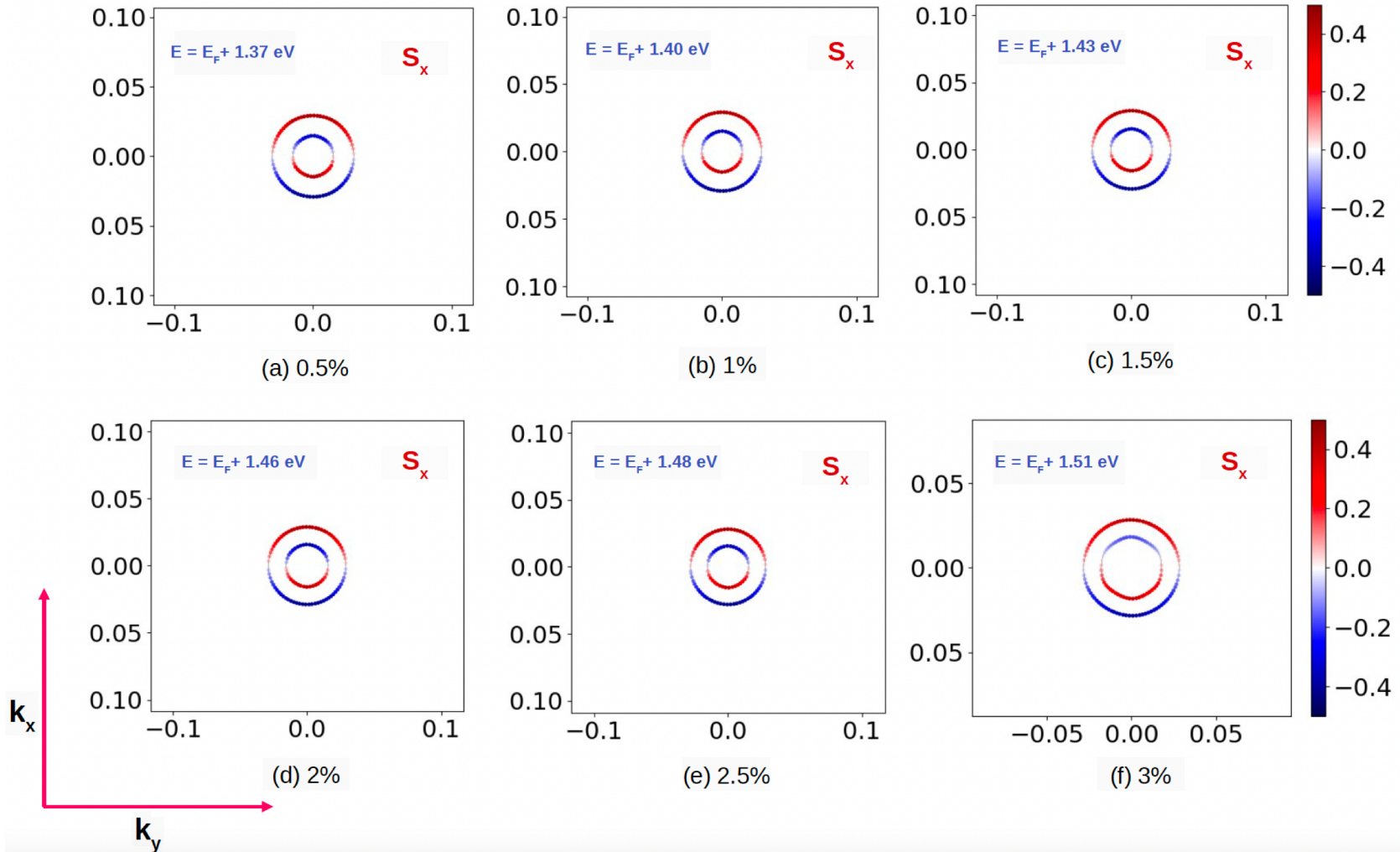


FIG. 3. Band structures of tensile strained BiClS monolayer obtained using PBE+SOC. Fig. (a) to (f) show the band structures of monolayer under the tensile strain from 0.5% to 3%. The valence band maxima is set to zero. The values with red (blue) color in all plots represent the bandgap and percentage of applied biaxial strain.

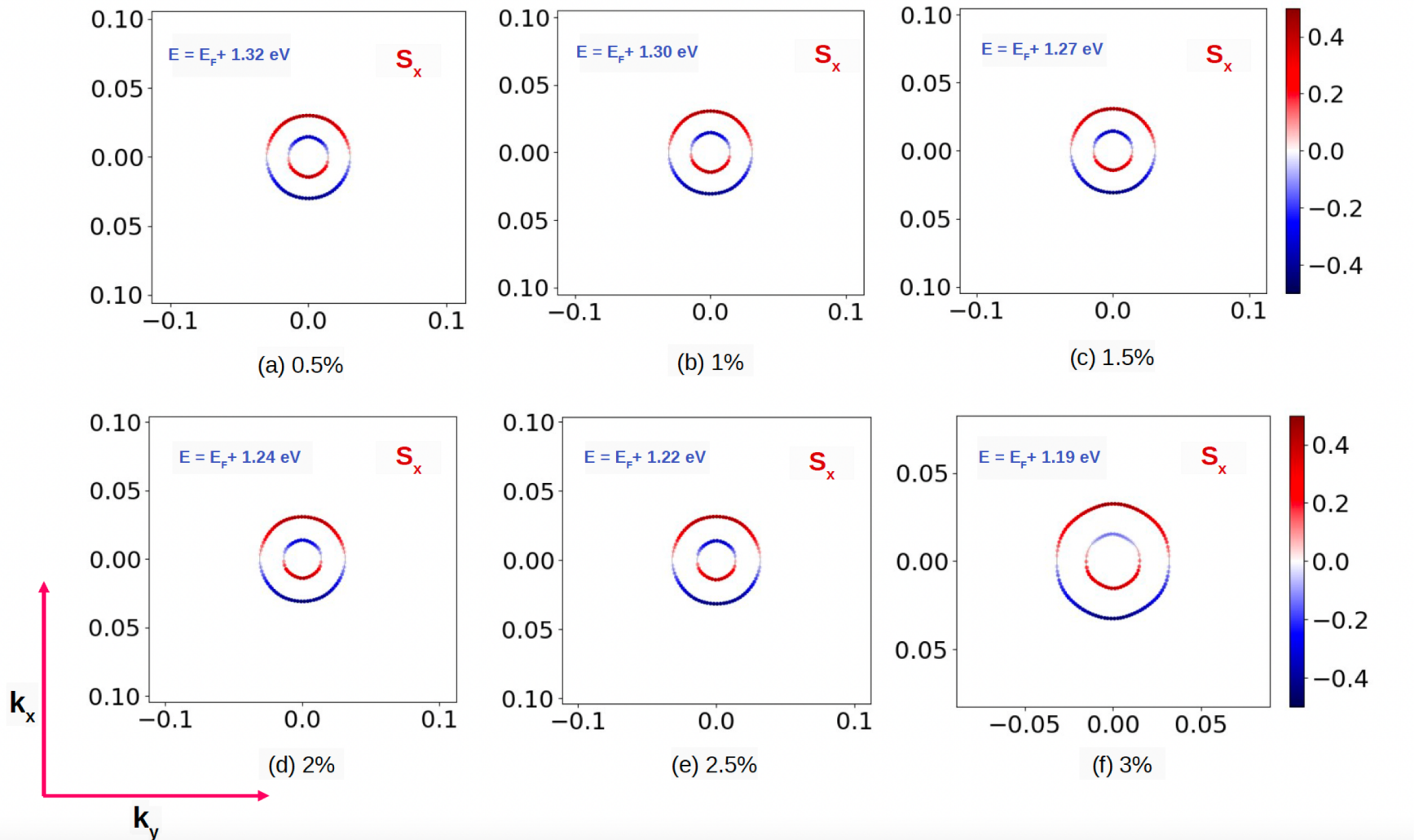
# Implication of Rashba Phenomena in 2D Materials

## Strain Induced Rashba Assisted Proton Reduction Tuning: BiClS Janus Monolayer

### Spin-Texture under compressive strain



### Spin-Texture under tensile strain



# Implication of Rashba Phenomena in 2D Materials

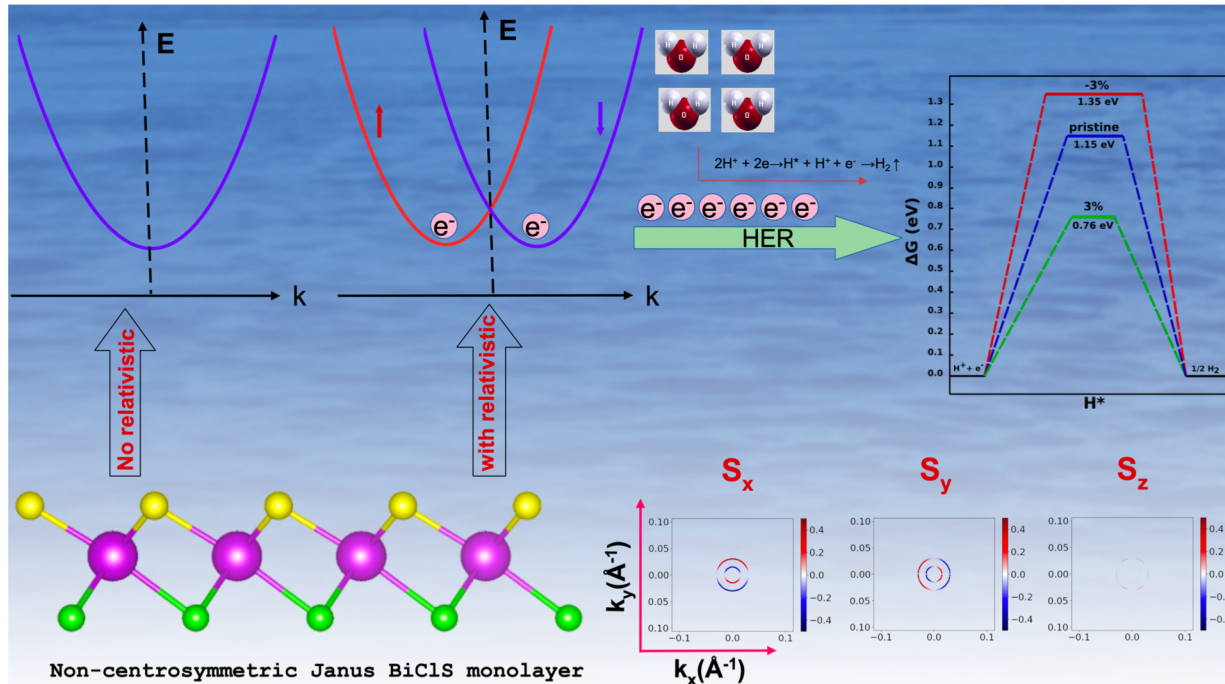
## Strain Induced Rashba Assisted Proton Reduction Tuning: BiClS Janus Monolayer

TABLE I. Bandgap of pristine and bi-axial strain induced Janus BiClS monolayer with PBE+SOC and HSE06+SOC consideration. The negative and positive value in column of strain denotes compressive and tensile strain. The last column contains formation energy ( $E_{\text{form}}$ )

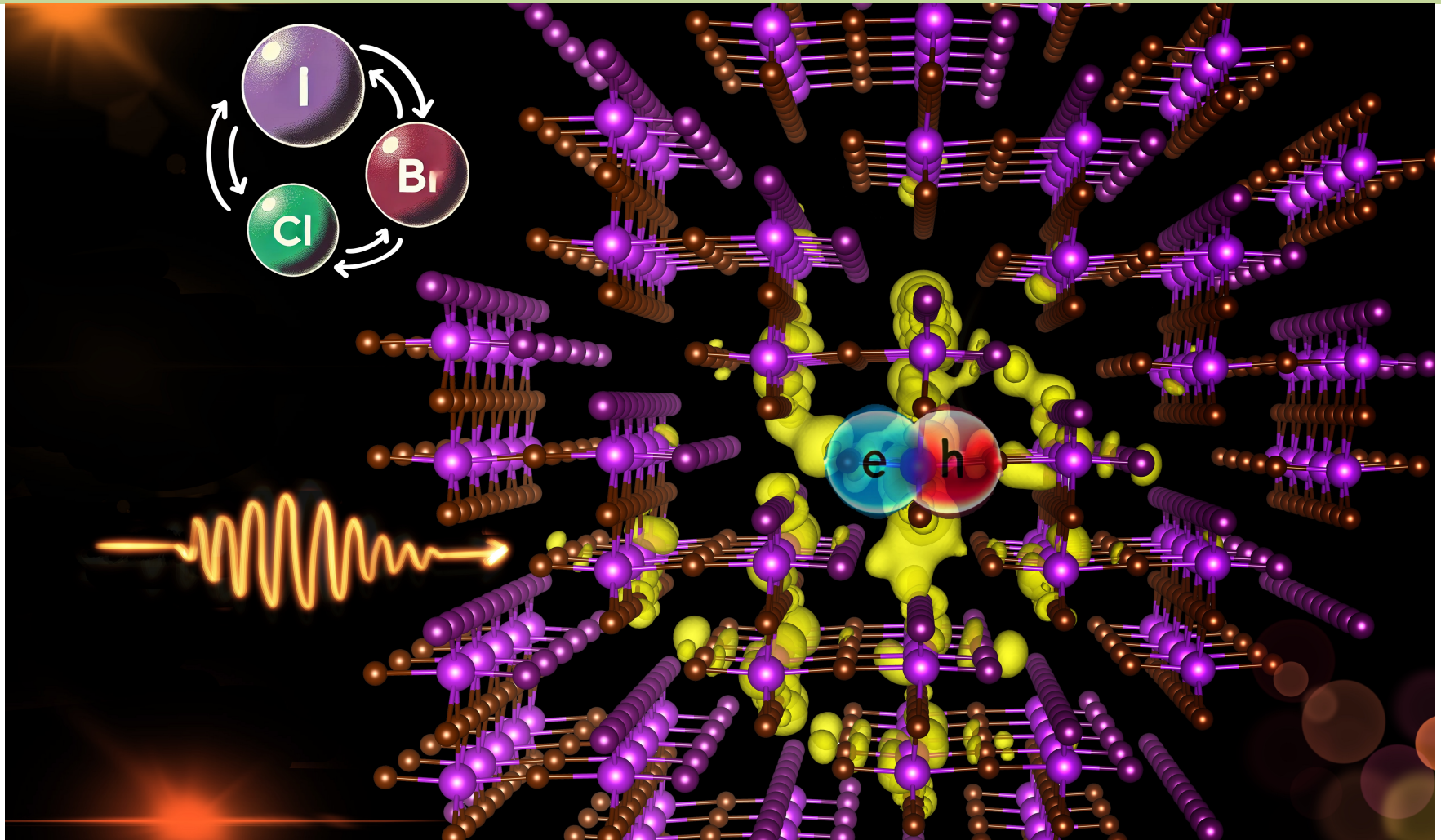
Strain(%)	PBE+SOC $E_g$ (eV)	HSE06+SOC $E_g$ (eV)	$E_{\text{form}}$ (eV/atom)
-0.5	1.36	2.02	-0.6745
-1.0	1.40	2.07	-0.6743
-1.5	1.43	2.08	-0.6734
-2.0	1.46	2.11	-0.7618
-2.5	1.48	2.14	-0.6695
-3.0	1.51	2.17	-0.6666
0.0	1.35	1.99	-0.6748
0.5	1.32	1.96	-0.6731
1.0	1.30	1.94	-0.6715
1.5	1.27	1.91	-0.6693
2.0	1.24	1.88	-0.6665
2.5	1.22	1.85	-0.6636
3.0	1.19	1.83	-0.6593

TABLE II. Rashba splitting  $\alpha_R$  determined using PBE+SOC and HSE06+SOC along  $\Gamma$ -M and  $\Gamma$ -K. The negative and positive value in first column denotes compressive and tensile strain.

Strain (%)	PBE+SOC		HSE06+SOC	
	$\Gamma$ -M	$\Gamma$ -K	$\Gamma$ -M	$\Gamma$ -K
-0.5	1.08	0.90	1.12	0.94
-1.0	1.00	0.82	1.04	0.86
-1.5	0.93	0.75	0.96	0.77
-2.0	0.85	1.35	0.87	0.68
-2.5	0.78	1.28	0.78	1.29
-3.0	0.70	1.21	0.69	1.21
0.0	1.16	0.99	1.22	1.04
0.5	1.22	1.05	1.25	1.10
1.0	1.28	1.11	1.35	1.17
1.5	1.34	1.17	1.43	1.26
2.0	1.41	1.25	1.50	1.33
2.5	1.47	1.30	1.57	1.40
3.0	1.52	1.36	1.10	1.47



# Can we establish a correlation between Rashba Splitting Strength and Excitonic Lifetime??



Transition Dipole

Exciton Energy

Radiative Recombination Rate  
of Specific Exciton State S  
in isotropic bulk crystal

$$\langle \gamma_S \rangle (T) = \frac{8\sqrt{\pi}\epsilon\epsilon_0 e^2 \hbar p_S^2}{3\epsilon_0 m^2 V E_S(0)^2} \left( \frac{E_S(0)^2}{2M_S m c^2 k_B T} \right)^{3/2}$$

Exciton Mass

# Excitonic Physics in Light-Matter Interactions (Treating Many Electrons with Many Body Perturbation Theory): GW & BSE

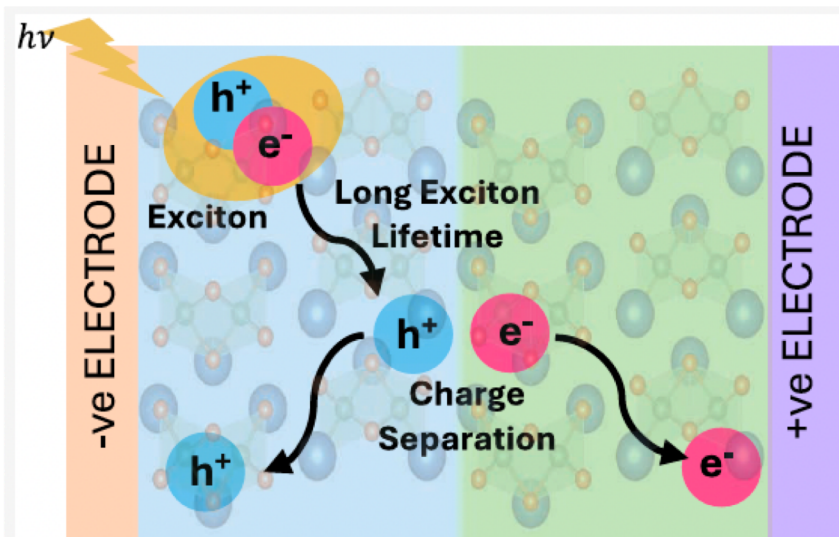
PHYSICAL REVIEW B **112**, 125107 (2025)

## Impact of strain on excitonic radiative lifetime in a polar $\text{Hf}_3\text{ZrS}_8$ monolayer: Theoretical insight based on many-body perturbation theory

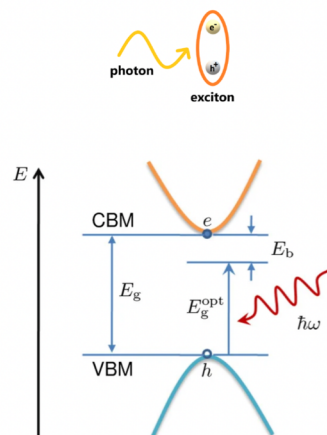
Dhirendra Kumar and Sudip Chakraborty

Materials Theory for Energy Scavenging Laboratory, Condensed Matter Physics, *Harish-Chandra Research Institute*,  
A C.I. of Homi Bhabha National Institute, Chhatnag Road, Jhansi, Prayagraj 211019, India

(Received 2 May 2025; revised 28 July 2025; accepted 5 August 2025; published 3 September 2025)



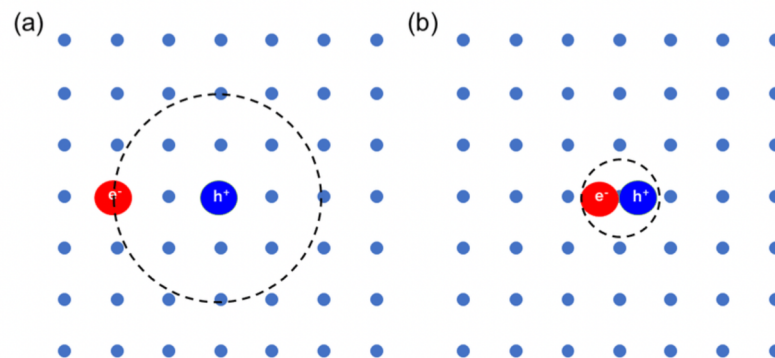
## Excitons?



- **Excitons** are charge-neutral quasiparticles that are formed in semiconductors and insulators upon absorption of photons.
- An exciton is made up of an electron and a hole that are bound together by a screened Coulomb interaction.
- The attraction between the electron and hole produces excitons with an energy  $E_{ex}$  that is lower than the quasiparticle (QP) band gap  $E_g^{QP}$ .

## Types of Excitons

- **Wannier-Mott excitons:** Delocalised states that can move freely throughout the crystal with large radius.
- **Frenkel excitons:** Localised states which are bound tightly with small radius.



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Article

## Exciton Delocalization and Excitonic Radiative Lifetime in Ternary Rhodium Halide Perovskites under Lattice Compression

Jagjit Kaur and Sudip Chakraborty\*

Cite This: <https://doi.org/10.1021/acs.jpcc.5c08785>

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# Excitonic Physics in Light-Matter Interactions (Treating Many Electrons with Many Body Perturbation Theory): GW & BSE

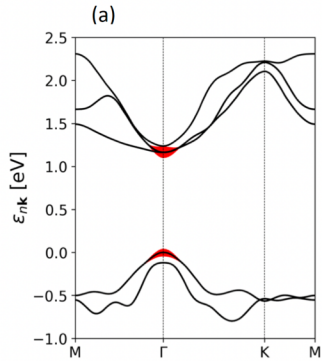
## First bright exciton wave function in Real and Reciprocal Space

- First bright exciton wave function spread in reciprocal space

- First bright exciton wave function spread in real space

$$|A_{eh}^\lambda\rangle, \text{ where } |\lambda\rangle = \sum_{eh} A_{eh}^\lambda |eh\rangle$$

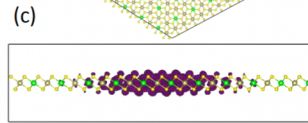
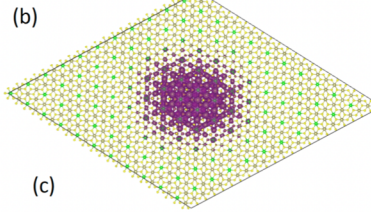
$$|\psi^S(r_e, r_h)\rangle = \sum_{cvk} A_{cvk}^S \psi_{ck}(r_e) \psi_{vk}^*(r_h)$$



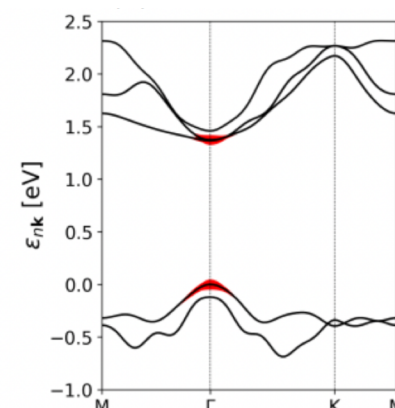
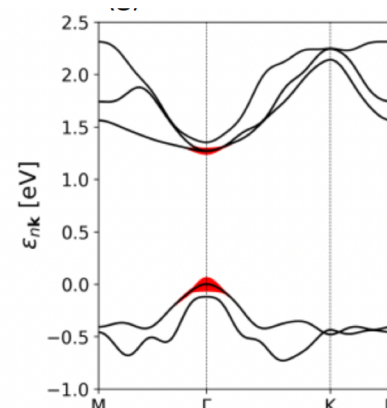
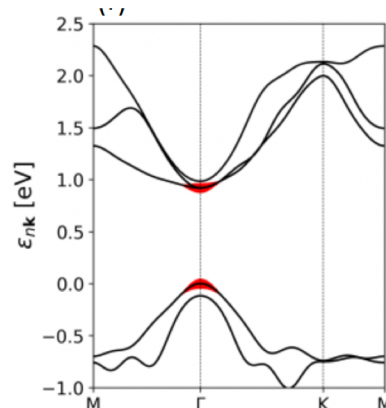
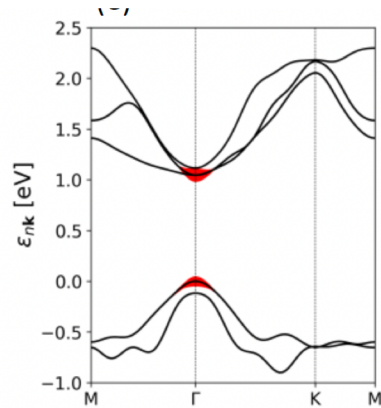
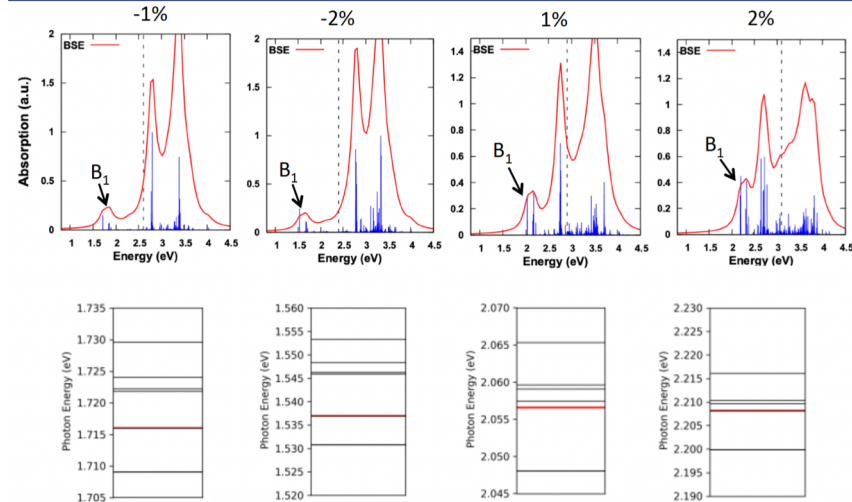
- Exciton formed by direct transition from VBM to CBM at  $\Gamma$  point.

- Hole position is fixed near to S atom.

- Exciton is more delocalised, confirm Wannier-Mott nature.



## Absorption Spectra Under Biaxial Strain

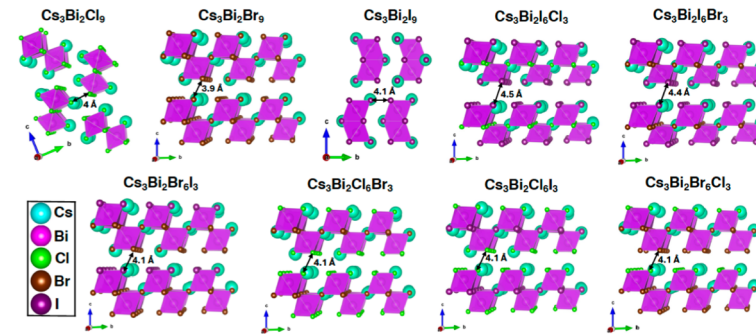


- The real space distribution is similar to that of the pristine one, as their binding energies are equivalent.

# Crossover of Frenkel and Wannier-Mott Excitons through Halide Composition Tuning in Mixed Halide Perovskites

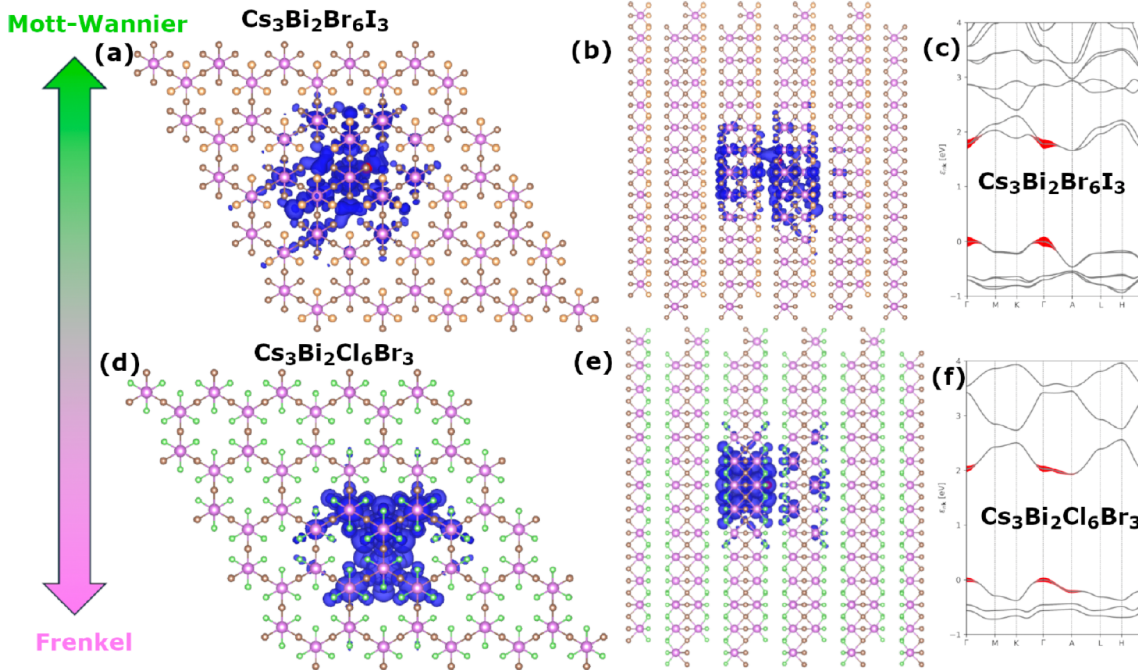
RESEARCH ARTICLE

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## Crossover of Frenkel and Wannier-Mott Excitons Through Halide Composition Tuning in Mixed Halide Perovskites

Jagjit Kaur and Sudip Chakraborty\*



System	$M_5^* (m_0)$		$\tau_{5K} (\mu s)$	
	Light	Heavy	Light	Heavy
$Cs_3Bi_2Cl_9$	0.40	0.94	4	14
$Cs_3Bi_2Br_9$	0.51	0.98	0.74	1.98
$Cs_3Bi_2I_9$	0.80	1.07	11	17
$Cs_3Bi_2I_6Cl_3$	0.39	1.19	1	5
$Cs_3Bi_2I_6Br_3$	0.93	1.44	7	14
$Cs_3Bi_2Br_6I_3$	3.64	4.50	24	33
$Cs_3Bi_2Cl_6Br_3$	0.36	0.84	0.33	1.20
$Cs_3Bi_2Cl_6I_3$	0.38	0.66	0.41	0.94
$Cs_3Bi_2Br_6Cl_3$	0.69	10.4	0.73	43

Square moduli of excitonic wavefunctions showing cross-over from Mott-Wannier type to Frenkel type of exciton

- (a) and (b): Top and Side perspective of  $Cs_3Bi_2Br_6I_3$   
 (d) and (e): Top and Side perspective of  $Cs_3Bi_2Cl_6Br_3$ .  
 (c) and (f) represents the first bright exciton located in the band structure.

# Towards Light Induced Superconductivity

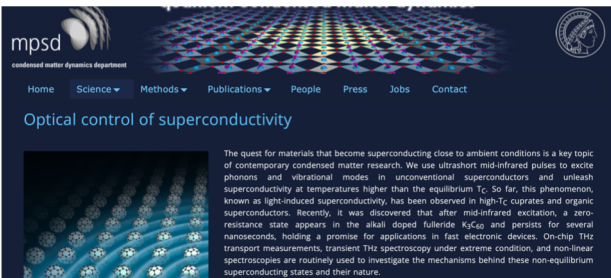
Quantum Electrodynamical DFT (QEDFT) for Strong Light Matter Interaction

*Origin of new Hybrid States - Polariton!*

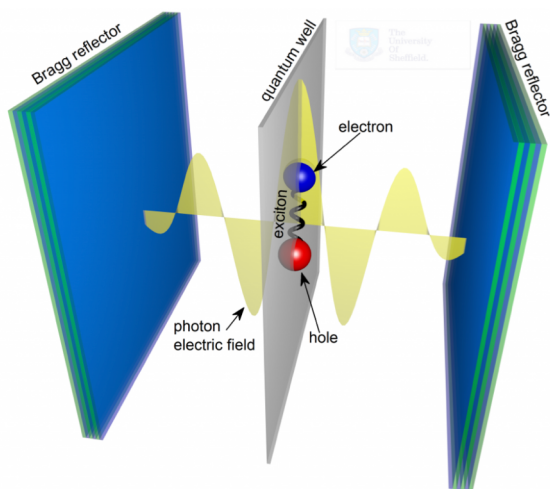
# Towards Light Induced Superconductivity

## Quantum Electrodynamical DFT (QEDFT) for Strong Light Matter Interaction

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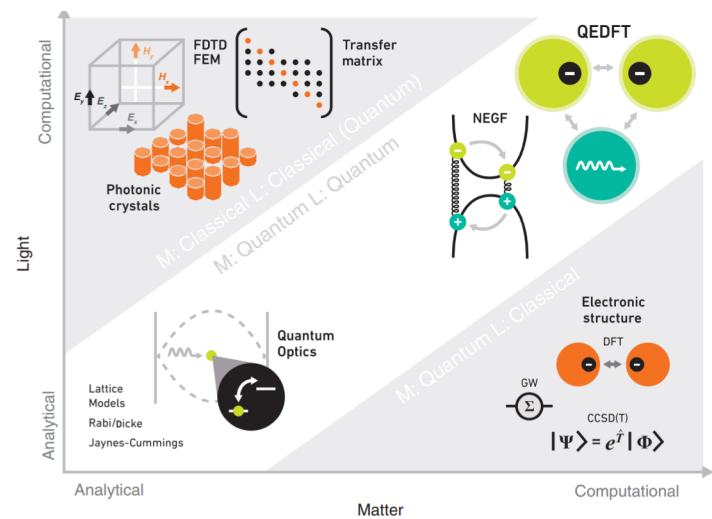
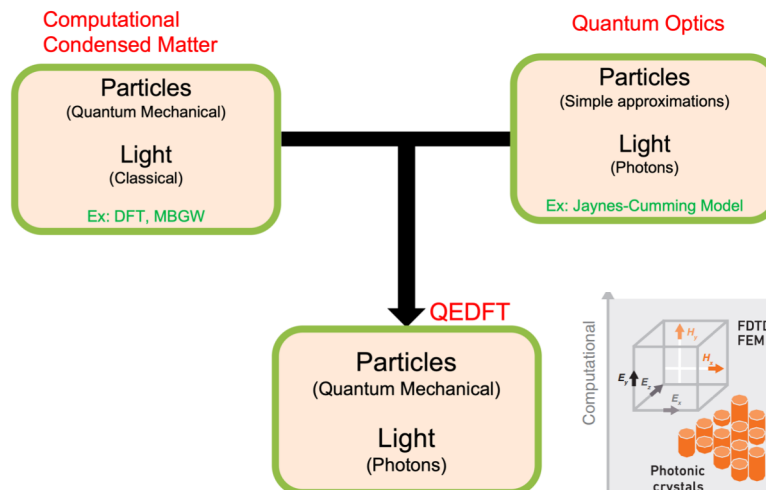
**Experimental Validation of Light Induced Superconductivity by Andrea Cavalleri, Director, Max Planck Hamburg, Germany**



nature physics ARTICLES  
<https://doi.org/10.1038/s41567-023-02235-9>  
**Resonant enhancement of photo-induced superconductivity in  $K_3C_{60}$**   
 Received: 18 January 2023 **E. Rowe<sup>1</sup>, B. Yuan<sup>1</sup>, M. Buzzì<sup>1</sup>, G. Jotzu<sup>1</sup>, Y. Zhu<sup>1</sup>, M. Fechner<sup>1</sup>, M. Först<sup>1</sup>, B. Liu<sup>2</sup>, D. Pontiroli<sup>3</sup>, M. Riccò<sup>3</sup> & A. Cavalleri<sup>1,4,5</sup>**  
 Accepted: 29 August 2023  
 Published online: 5 October 2023  
 Check for updates

Photo-excitation at terahertz and mid-infrared frequencies has emerged as an effective way to manipulate functionalities in quantum materials, in some cases creating non-equilibrium phases that have no equilibrium

nature physics ARTICLES  
<https://doi.org/10.1038/s41567-018-0134-8>  
**Pressure tuning of light-induced superconductivity in  $K_3C_{60}$**   
 A. Cantaluppi<sup>1,2,6</sup>, M. Buzzì<sup>1,6</sup>, G. Jotzu<sup>1</sup>, D. Nicoletti<sup>1,2</sup>, M. Mitrano<sup>1</sup>, D. Pontiroli<sup>3</sup>, M. Riccò<sup>3</sup>, A. Perucchi<sup>4</sup>, P. Di Pietro<sup>4</sup> and A. Cavalleri<sup>1,2,5\*</sup>  
 Corrected: Publisher Correction



# Electron-Phonon Physics and the repercussion on Superconductivity

PHYSICAL REVIEW B 00, 004500 (2025)

## Pressure induced evolution of anisotropic superconductivity and Fermi surface nesting in a ternary boride

Subhajit Pramanick<sup>1,\*</sup>, Sudip Chakraborty<sup>2,†</sup> and A. Taraphder<sup>1,‡</sup>

<sup>1</sup>Department of Physics, Indian Institute of Technology Kharagpur, Kharagpur 721302, India

<sup>2</sup>Materials Theory for Energy Scavenging Lab, Harish-Chandra Research Institute, A CI of Homi Bhabha National Institute, Chhatnag Road, Jhansi, Prayagraj 211019, India

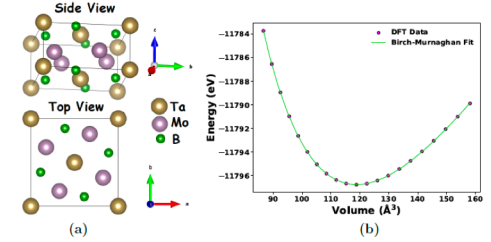


FIG. 1. (a) Crystal structure of Ta(MoB)<sub>2</sub> at ambient pressure, (b) Birch-Murnaghan equation fitting for finding bulk modulus and its pressure derivative

## Phonon-mediated Superconductivity

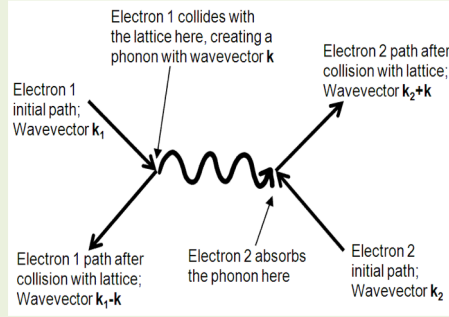
### BCS theory

- Attractive electron - electron interaction mediated by phonon → Cooper pairs

- $T_c$  can be calculated from:

$$T_c = 1.14 \theta_D \exp\left(-\frac{1}{N(0)V}\right)$$

- Does not account for the retardation of the el-ph interaction, Fails to explain anisotropic superconductivity etc.



### Allen-Dynes modified McMillan formula

- $T_c$  can be calculated from:

$$T_c = \frac{\omega_{log}}{1.20} \exp\left[\frac{-1.04(1+\lambda)}{\lambda - \mu_c^2(1+0.62\lambda)}\right]$$

- Isotropic Eliashberg spectral functions and EPC strength are:

$$\alpha^2F(\omega) = \frac{1}{N_F} \sum_{nmv} \int \frac{dk}{\Omega_{BZ}} \frac{dq}{\Omega_{BZ}} |g_{mnu}(k, q)|^2 \times \delta(\omega - \omega_{qv}) \times \delta(\epsilon_{nk} - \epsilon_F) \times \delta(\epsilon_{mk+q} - \epsilon_F)$$

$$\text{and } \lambda = 2 \int \frac{\alpha^2F(\omega)}{\omega} d\omega$$

- Needs dense k- and q- meshes to converge  $\lambda$ , Fails for multiband and/or anisotropic Superconductivity

### Migdal-Eliashberg Formalism

- Solve ME equations self-consistently:

$$Z(k_1, i\omega_{n_1}) = 1 + \frac{\pi T}{N_F \omega_{n_1}} \sum_{k_2 n_2} \frac{\omega_{n_2}}{\sqrt{\omega_{n_2}^2 + \Delta^2(k_2, i\omega_{n_2})}} \lambda(k_1, k_2, n_1 - n_2) \delta(\epsilon_{k_2})$$

$$\Delta(k_1, i\omega_{n_1}) \Delta(k_1, i\omega_{n_1}) = \frac{\pi T}{N_F} \sum_{k_2 n_2} \frac{\Delta(k_2, i\omega_{n_2})}{\sqrt{\omega_{n_2}^2 + \Delta^2(k_2, i\omega_{n_2})}} \times [\lambda(k_1, k_2, n_1 - n_2) - N_F V(k_1 - k_2)] \delta(\epsilon_{k_2})$$

- Anisotropic Eliashberg spectral function and EPC strength are:

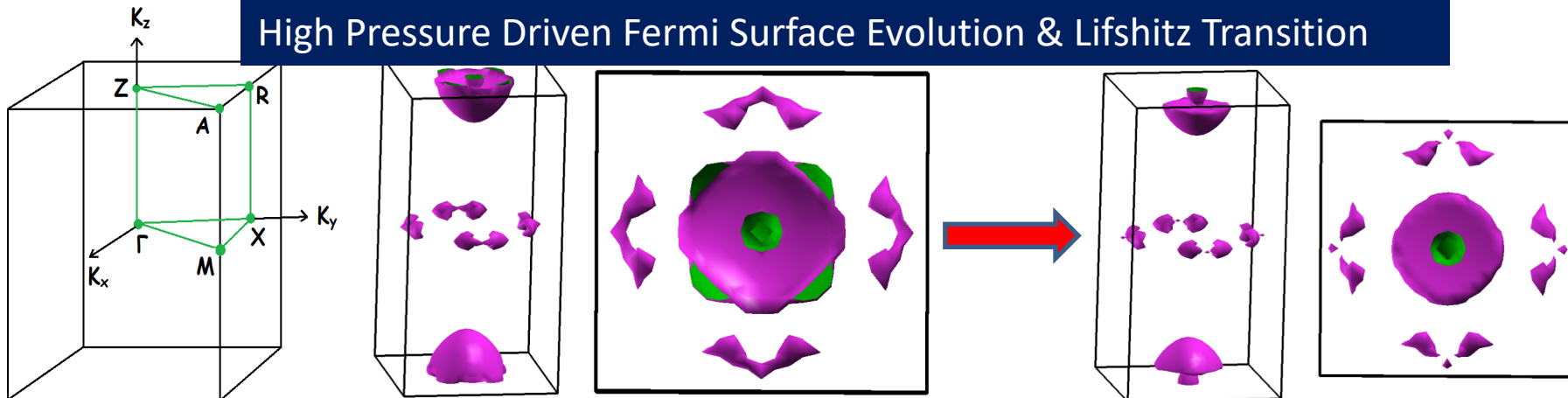
$$\alpha^2F(k_1, k_2, \omega) = N_F \sum_v |g_{mnu}^{SE}(k, q)|^2 \delta(\omega - \omega_{k_1 - k_2, v}) \text{ and } \lambda(k_1, k_2, n_1 - n_2) = \int_0^\infty d\omega \frac{2\omega}{(\omega_{n_1} - \omega_{n_2})^2 + \omega^2} \alpha^2F(k_1, k_2, \omega)$$

- Solve Z and  $\Delta$  along imaginary energy axis for each Matsubara frequency → solve it along real energy axis via analytic continuation → obtain quasiparticle energy from poles of the normal Green's function

$$G(k, \omega) = \frac{\omega Z(k, \omega) + \epsilon_k}{[\omega Z(k, \omega)]^2 - \epsilon_k^2 - [Z(k, \omega) \Delta(k, \omega)]^2} \text{ and } E_k^2 = \left[\frac{\epsilon_k}{Z(k, E_k)}\right]^2 + \Delta^2(k, E_k)$$

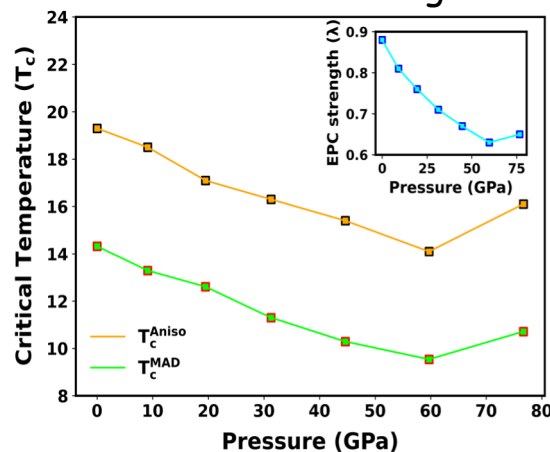
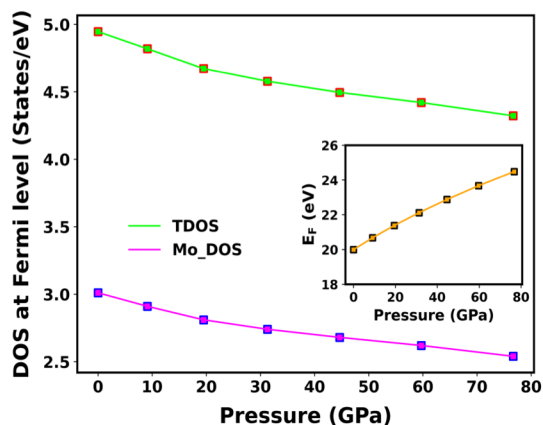
- Have taken retardation into account, Captures anisotropic superconductivity, Neglect non-adiabatic effects (Migdal theorem)

## High Pressure Driven Fermi Surface Evolution & Lifshitz Transition



□ What happens if we apply external hydrostatic pressure?

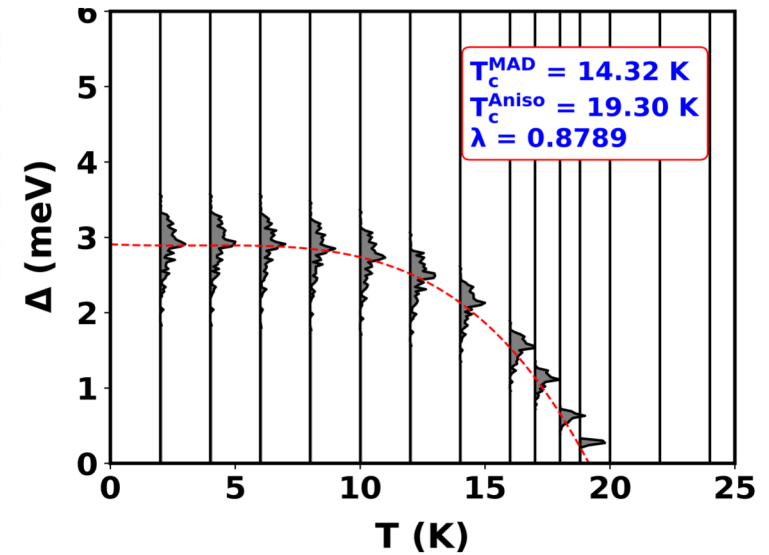
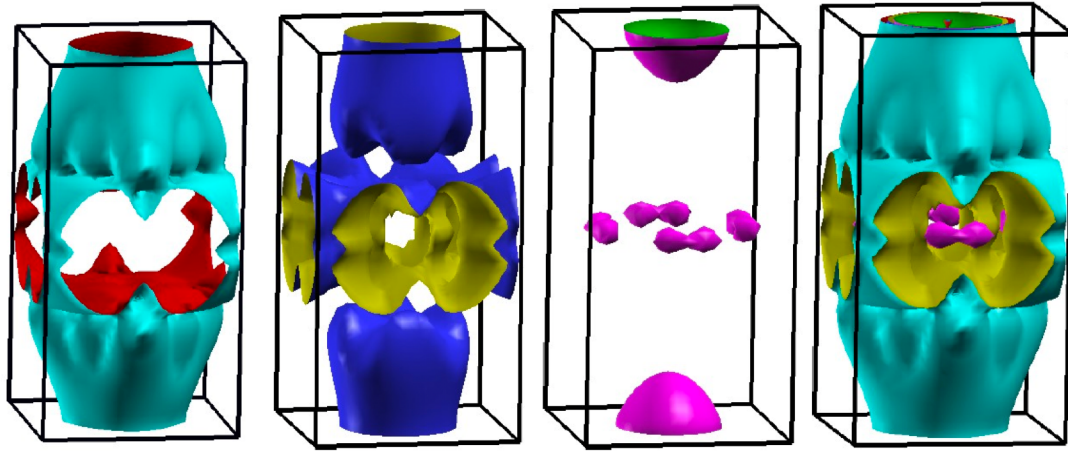
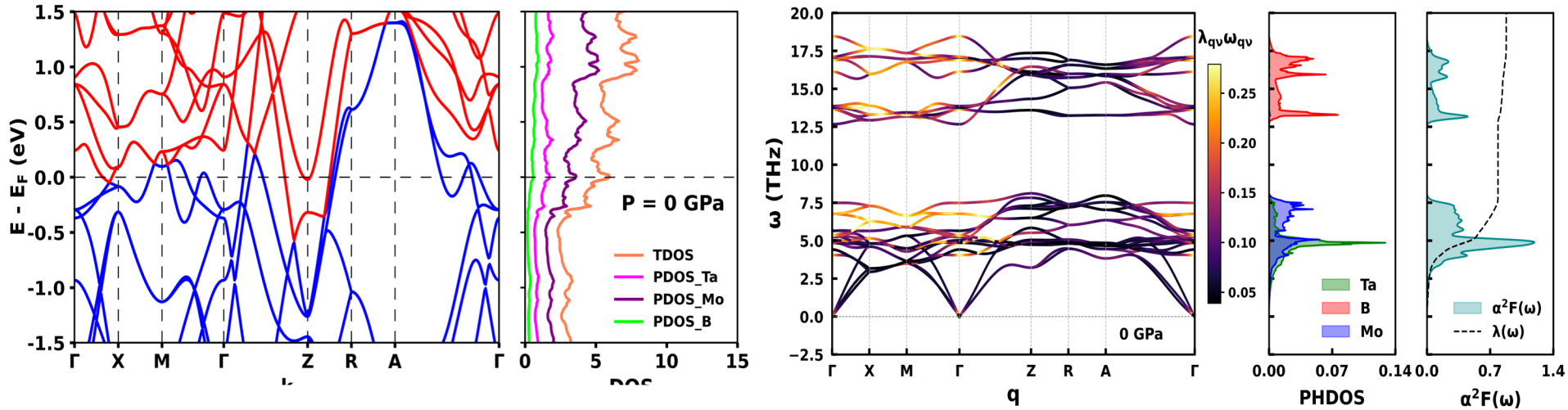
□ A topological change of the Fermi surface  $\rightarrow$  Lifshitz transition occurring at 76.69 GPa



□ Decrease in DOS at FL, peak of the nesting function and increase in phonon frequency  $\rightarrow$  Reduction of  $\lambda$  and  $T_c$  with pressure up to 59.71 GPa

□ Lifshitz transition induced enhanced nesting  $\rightarrow$  sudden increase of  $\lambda$  and  $T_c$  at 76.69 GPa

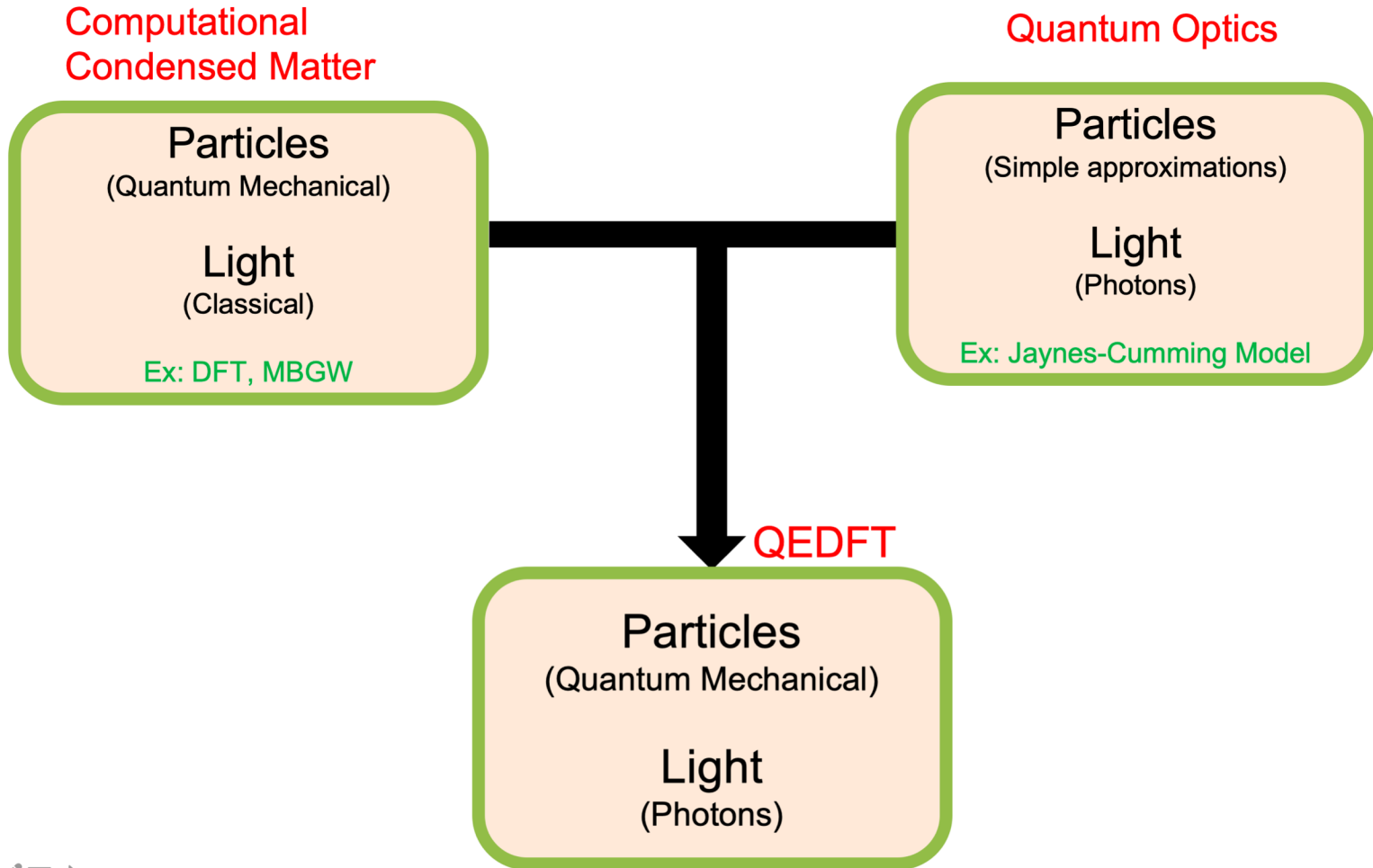
# Other Thrust Area: Electron-Phonon Physics and the repercussion on Superconductivity



- ❑ Four bands at the Fermi level → d-orbital characteristics
- ❑ Phonon modes from acoustic and optical branch along  $\Gamma \rightarrow X \rightarrow M \rightarrow \Gamma$  contribute in superconductivity
- ❑ Single gap anisotropic phonon mediated superconductor having  $\lambda = 0.88$ ,  $T_c^{\text{Aniso}} = 19.30 \text{ K}$

# Towards Light Induced Superconductivity

## Quantum Electrodynamical DFT (QEDFT) for Strong Light Matter Interaction



# Acknowledgements



**Webpage:** <https://www.hri.res.in/~sudipchakraborty/>



*Thank you for listening*

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Sankalpa Bora (DST Solar JRF)

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## Ph.D. Alumni of MATES Lab

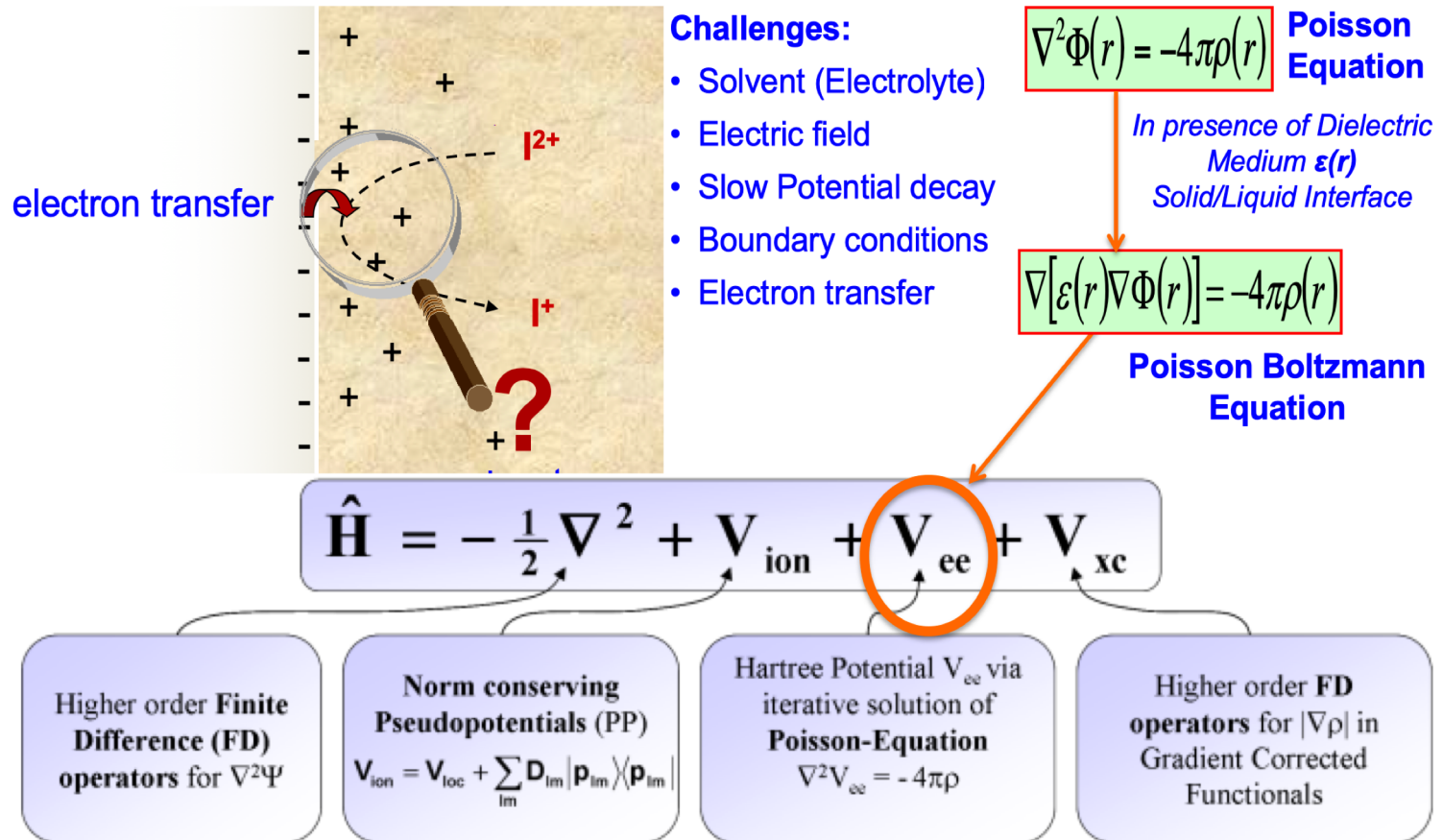
**Dr. Amitava Banerjee**, Assistant Professor, IIT Jodhpur

**Dr. Vivekanand Shukla**, Assistant Professor, IIT Ropar

**Dr. Teeraphat Watachatharapong**, Faculty at Kasetsart University

**Dr. Rafael Araujo**, Senior Researcher, Uppsala university, Sweden

# In-house Code Development for Non-linear Poisson Boltzmann Solver



Development of Standalone Poisson-Boltzmann Solver

# In-house Code Development relevant to Energy Materials

Development & Applications of Transition Pathway Prediction Method  
DFT + Hybrid Eigen-vector Following (EF) Interface

**cm** CHEMISTRY OF MATERIALS

Article  
pubs.acs.org/cm

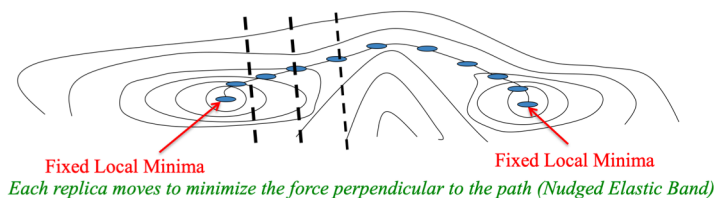
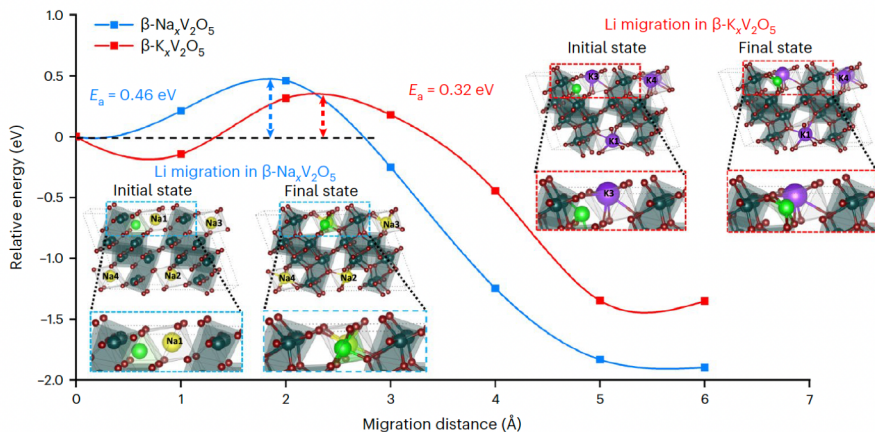
## Mapping Structural Changes in Electrode Materials: Application of the Hybrid Eigenvector-Following Density Functional Theory (DFT) Method to Layered $\text{Li}_{0.5}\text{MnO}_2$

Ieuan D. Seymour,<sup>†</sup> Sudip Chakraborty,<sup>‡</sup> Derek S. Middlemiss,<sup>§</sup> David J. Wales,<sup>†</sup> and Clare P. Grey<sup>\*,†</sup>

Our newly developed interface for Unbiased Transition Pathway Prediction is available (svn version under GPL)

@

<http://www-wales.ch.cam.ac.uk/OPTIM>

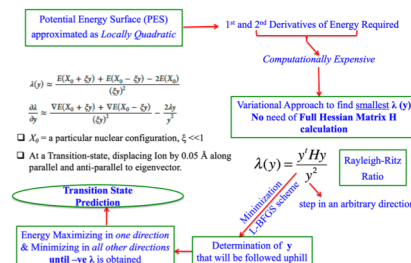


The Bottleneck

- ❖ Cooperative Nature of Many Transitions
- ❖ Multiple Atoms & Large System Requirement
- ❖ Need to know Start & End points

Single-ended Hybrid Eigenvector Following (EF)

+  
DFT



More accurate determination of Ion Migration

Kinetic Stability of Metastable State

nature materials

Article

<https://doi.org/10.1038/s41563-024-01842-y>

## Effect of pre-intercalation on Li-ion diffusion mapped by topochemical single-crystal transformation and operando investigation

Received: 26 February 2022

Accepted: 19 February 2024

Published online: 21 March 2024

Yuting Luo<sup>1,2,6</sup>, Joseph V. Handy<sup>1,2,6</sup>, Tisita Das<sup>3,6</sup>, John D. Ponis<sup>1,2,6</sup>, Ryan Albers<sup>1,2</sup>, Yu-Hsiang Chiang<sup>1,2</sup>, Matt Pharr<sup>4</sup>, Brian J. Schultz<sup>2</sup>, Leonardo Gobatto<sup>5</sup>, Dean C. Brown<sup>5</sup>, Sudip Chakraborty<sup>3,5</sup> & Sarbjit Banerjee<sup>1,2</sup>

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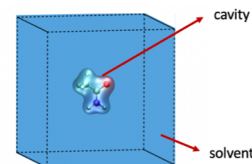
**Dr. Rafael Araujo**, Senior Researcher, Uppsala university, Sweden

# Electronic Structure Codes (Density Functional Theory Formalism based codes)

## VASP - Vienna Ab-initio Simulation Package (Fourier-space DFT)

- Accurate Structure Relaxation with Spin-orbit Coupling (SOC) and (vdW) dispersion.
- Density of States and Optical Response with GGA+U, HSE06 (Hybrid) **Functional**
- Free Energy based **Reaction Coordinate** of Catalytic Reactions (HER/OER/ORR)

Implicit model for plane wave DFT



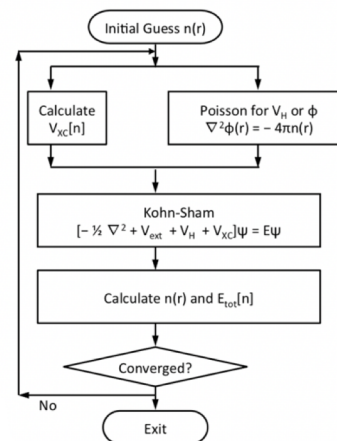
## Phonopy (Phonon Dispersions)

- Dynamical Stability based on Phonon Dispersion
- Thermal Properties (**Heat Capacity, Free Energy, Thermal Expansion**)
- Bulk Modulus ( $B_0$ ) and Elastic Moduli

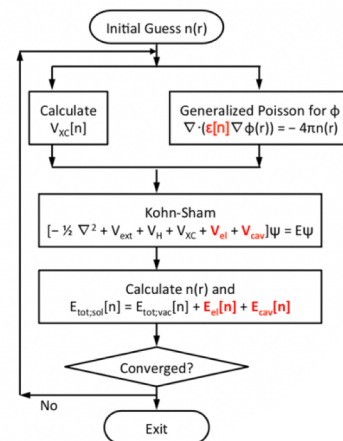
## GPAW - Grid-based projector Augmented Wave (Real Space DFT)

- X-ray Absorption (XAS), Emission (XES), EELS
- TDDFT based Dielectric Response, More Accurate  $E_{\text{gap}}$
- Implementing Poisson Boltzmann Solver

### Gas Phase Calculation



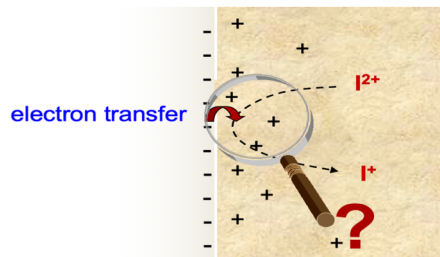
### Solvation Calculation



Our newly developed interface for Unbiased Transition Pathway Prediction is available (svn version under GPL)

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<http://www.wales.ch.cam.ac.uk/OPTIM>



### Challenges:

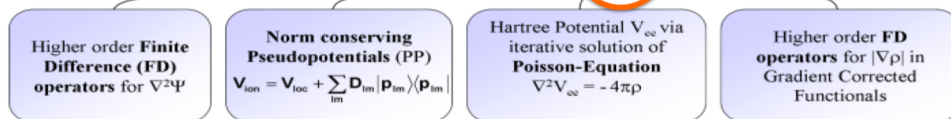
- Solvent (Electrolyte)
- Electric field
- Slow Potential decay
- Boundary conditions
- Electron transfer

$$\nabla^2 \Phi(r) = -4\pi \rho(r) \quad \text{Poisson Equation}$$

In presence of Dielectric Medium  $\epsilon(r)$  Solid/Liquid Interface

$$\nabla \cdot [\epsilon(r) \nabla \Phi(r)] = -4\pi \rho(r) \quad \text{Poisson Boltzmann Equation}$$

$$\hat{H} = -\frac{1}{2} \nabla^2 + V_{\text{ion}} + V_{\text{ee}} + V_{\text{xc}}$$



Development of Standalone Poisson-Boltzmann Solver

# Excitonic Physics in Light-Matter Interactions

## (Treating Many Electrons with Many Body Perturbation Theory): GW & BSE

### Quasiparticle Energy Corrections

- DFT as starting point for the GW approximation, in the single shot  $G_0W_0$  the electronic self energy

$$\Sigma(r, r', \omega) = \frac{i}{2\pi} \int G_0(r, r', \omega + \omega') W_0(r, r', \omega') e^{i\omega'\eta} d\omega'$$

- $G_0$  is the single-particle Green's function
- $W_0$  is the Coulomb potential

$$(W_0 = \epsilon^{-1}v)$$

- Quasiparticle energy within  $G_0W_0$  approach: Plasmon Pole Approximation

$$E_{nk}^{QP} = \epsilon_{nk} + Z_{nk} \left[ \sum_{nk} (\epsilon_{nk}) - V_{nk}^{xc} \right]$$

$Z_{nk} \rightarrow$  renormalization factor

$$Z_{nk} = \left[ 1 - \frac{d \sum_{nk}(\omega)}{d\omega} \Big|_{\omega=\epsilon_{nk}} \right]^{-1}$$

### Excitonic properties

- Bethe-Salpeter Equation (BSE) in matrix form

$$\begin{pmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{B}^* & \mathbf{A}^* \end{pmatrix} \begin{pmatrix} \mathbf{X}_S \\ \mathbf{Y}_S \end{pmatrix} = \Omega_S \begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix} \begin{pmatrix} \mathbf{X}_S \\ \mathbf{Y}_S \end{pmatrix}$$

where  $\mathbf{A}$  is the excitation,  $\mathbf{B}$  is the coupling between excitation and de-excitations

- Bethe-Salpeter Equation (BSE) within the **Tamm-Dancoff** approximation, means  $\mathbf{B}$  is set to zero

$$(E_{c\mathbf{k}} - E_{v\mathbf{k}}) A_{v\mathbf{c}\mathbf{k}}^S + \sum_{\mathbf{k}'v'c'} \langle v\mathbf{c}\mathbf{k} | K_{eh} | v'\mathbf{c}'\mathbf{k}' \rangle A_{v'\mathbf{c}'\mathbf{k}'}^S = \Omega^S A_{v\mathbf{c}\mathbf{k}}^S \quad \longrightarrow (1)$$

$E_{c\mathbf{k}}, E_{v\mathbf{k}}$  Single-(quasi)particle energies,  $\Omega^S$  Exciton energy (eigenvalues)

$A_{v\mathbf{c}\mathbf{k}}^S$  Exciton amplitude (eigenvectors)  $K_{eh}$  Electron-hole kernel

- Exciton radiative lifetime at zero temperature:

$$\tau_S(0) = \gamma_S(0)^{-1} = \frac{\epsilon_0 \hbar^2 c A_{uc}}{e^2 E_S(0) \mu_S^2}$$

- Exciton radiative lifetime at non-zero temperature:

$$\langle \tau_S \rangle(T) = \gamma_S(0)^{-1} \times \frac{3}{4} \left[ \frac{2M_S^* c^2 k_B T}{E_S(0)^2} \right]$$

$\mu_S^2$  Exciton transition dipole moment matrix

$A_{uc}$  Area of unit cell

$E_S(0)$  Energy of first bright exciton

$M_S^*$  Exciton effective mass

- Types of excitons—

- Dark excitons—optically inactive—oscillation strength equivalent to zero
- Bright excitons—optically active—finite oscillation strength

- Exciton binding energy defines the strength, which is difference between bandgap and exciton energy.

# Excitonic Physics in Light-Matter Interactions

## (Treating Many Electrons with Many Body Perturbation Theory): GW & BSE

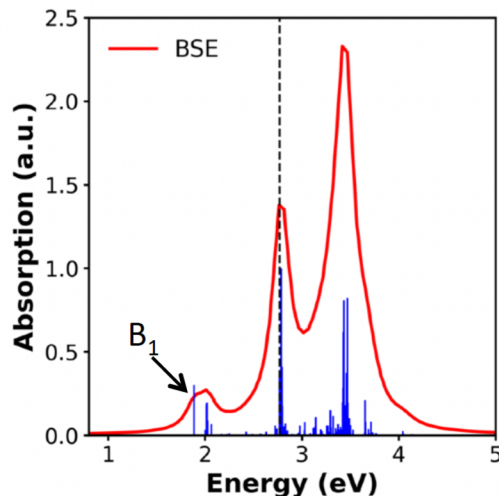
### Optical Absorption Spectra, BSE+G<sub>0</sub>W<sub>0</sub>

**Note-** As we used truncated Coulomb potential, the imaginary part of the dielectric function become zero.

- Optical absorption spectra are calculated from imaginary part of macroscopic polarisability, with long-wavelength limit ( $q \rightarrow 0$ )

$$\text{Im}[\alpha_M^{2D}(\omega)] = \frac{2\pi^2 e^2}{A\omega^2} \sum_S \left| \sum_{v,c,\mathbf{k}} A_S^{vck} \langle v\mathbf{k} | \hat{v}_\mu | c\mathbf{k} \rangle \right|^2 \delta(\omega - \Omega_S) \longrightarrow (2)$$

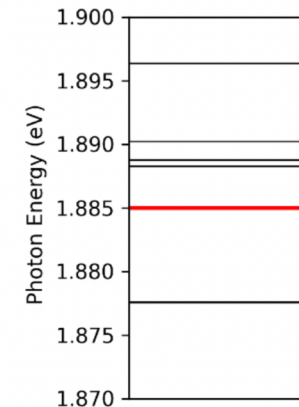
$\hat{v}_\mu$  Velocity operator along the direction of polarization



- Blue solid lines represent the exciton oscillation strength.

$$\left| \sum_{cv\mathbf{k}} A_{cv\mathbf{k}}^S \langle c\mathbf{k} | \hat{v}_\mu | v\mathbf{k} \rangle \right|^2$$

Linear combination of the square of the dipole transition matrix elements



Black lines — Dark excitons  
Red lines — Bright excitons

- $B_1$  is first bright exciton
- Energy of  $B_1 = 1.885$  eV (optical gap)
- $E_b = 0.88$  eV

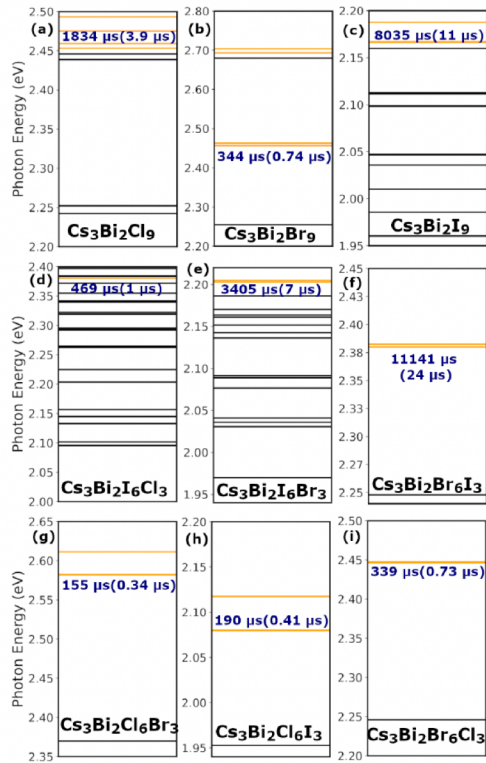
- Exciton binding energy

$$E_b = E_g^{G_0W_0+SOC} - E_g^{opt}$$

### Exciton Fine Structures

# Can we establish a correlation between Rashba Splitting Strength and Excitonic Lifetime??

## Exciton Fine Structure



Radiative recombination rate<sup>1</sup> of a specific exciton state  $S$  at temperature  $T$ :

$$\langle \gamma_S \rangle (T) = \frac{8\sqrt{\pi}\epsilon\epsilon_0 e^2 \hbar p_S^2}{3\epsilon_0 m^2 V E_S(0)^2} \left( \frac{E_S(0)^2}{2M_S m c^2 k_B T} \right)^{3/2}$$

- $E_S(0)$  - exciton energy
- $p_S$  - transition dipole
- $M_S$  - exciton mass,  $M_S = m_e^* + m_h^*$ .
- Radiative lifetime is  $\langle \tau_S \rangle = \langle \gamma_S \rangle^{-1}$

<sup>1</sup>H.-Y. Chen, V. A. Jhalani, M. Palummo, and M. Bernardi, Ab initio calculations of exciton radiative lifetimes in bulk crystals, nanostructures, and molecules, Phys. Rev. B 100, 075135 (2019)