Master Project Final Report

First-principles studies of quantum defect candidates in 2D WS2

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18/06/2024

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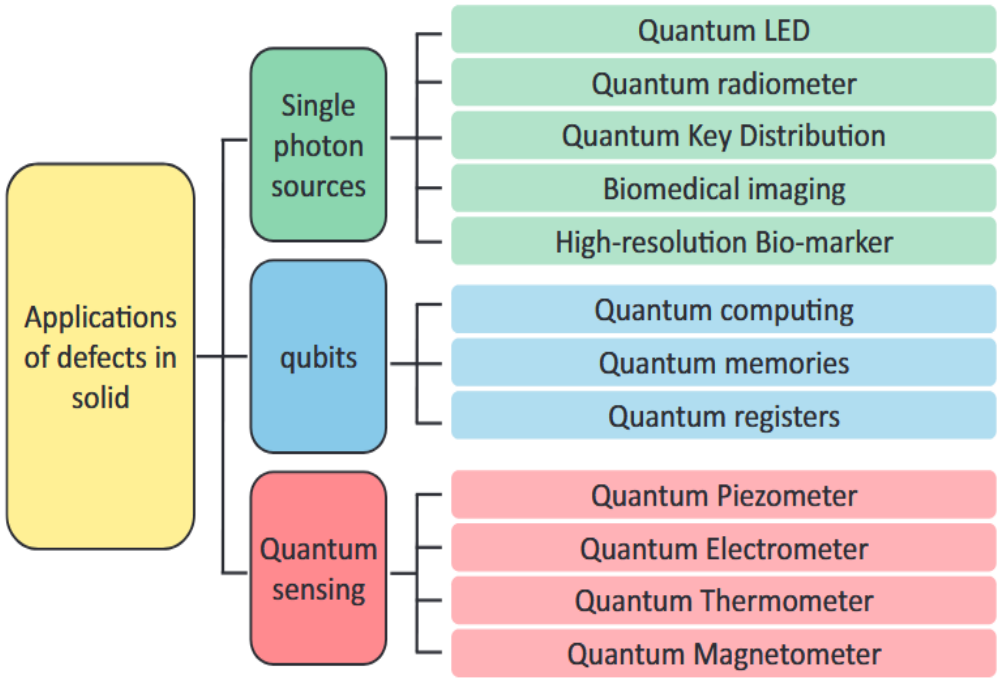
Background

Quantum point defect



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Background

Quantum point defect in 2D material

Controllable Defect Positions: Current experimental techniques enabling nearly deterministic defect positions. Also, strain, electric and magnetic fields can be intentionally engineered.

Stacking: 2D materials offer substantial flexibility in forming multi-layer structures . The layer-dependent electronic structures and interlayer couplings provide opportunities by incorporat - ing an atom or molecule between layers

Surface: 2D materials inherently serve as excellent platforms for quantum sensing due to their surface properties. The embedding of SPEs in monolayers circumvents issues like total internal reflection common in 3D color centers, significantly improving light extraction effi- ciency.

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Background

Key quantities

Category	Defect properties
Basic ground-state properties	Geometries, defect formation energies, charge-state transition levels, ground-state spin multiplicity
Specific ground-state properties	Magnetic interactions (zero-field splitting, spin-orbit, hyperfine), vibrational modes and frequencies, electron-phonon coupling, spin-phonon coupling
Excited-state properties	Excited-state energies and geometries, multiplet structure, transition dipole moments, radiative rates, optical lineshapes, nonradiative transitions

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Background

Defects as spin qubits

- **Deep defect levels:** Enhance the fidelity of stored quantum information. To prevent resonance with pristine band edges, quantum defects should have energy levels distinctly separated from the band edges.
- **High spin states:** Essential for the initialization, operation, and readout of spin qubits. The simplest example of this would be two parallel unpaired spins.
- **Radiative recombination rate:** Should be greater than the non-radiative rate, it ensures effective readout of spin qubits.
- **Weak coupling with environmental factors:** When there's limited interaction with elements like phonons and nuclear spins, spin lifetime at room temperature is extended. This improves the duration of stored information and reduces qubit errors.

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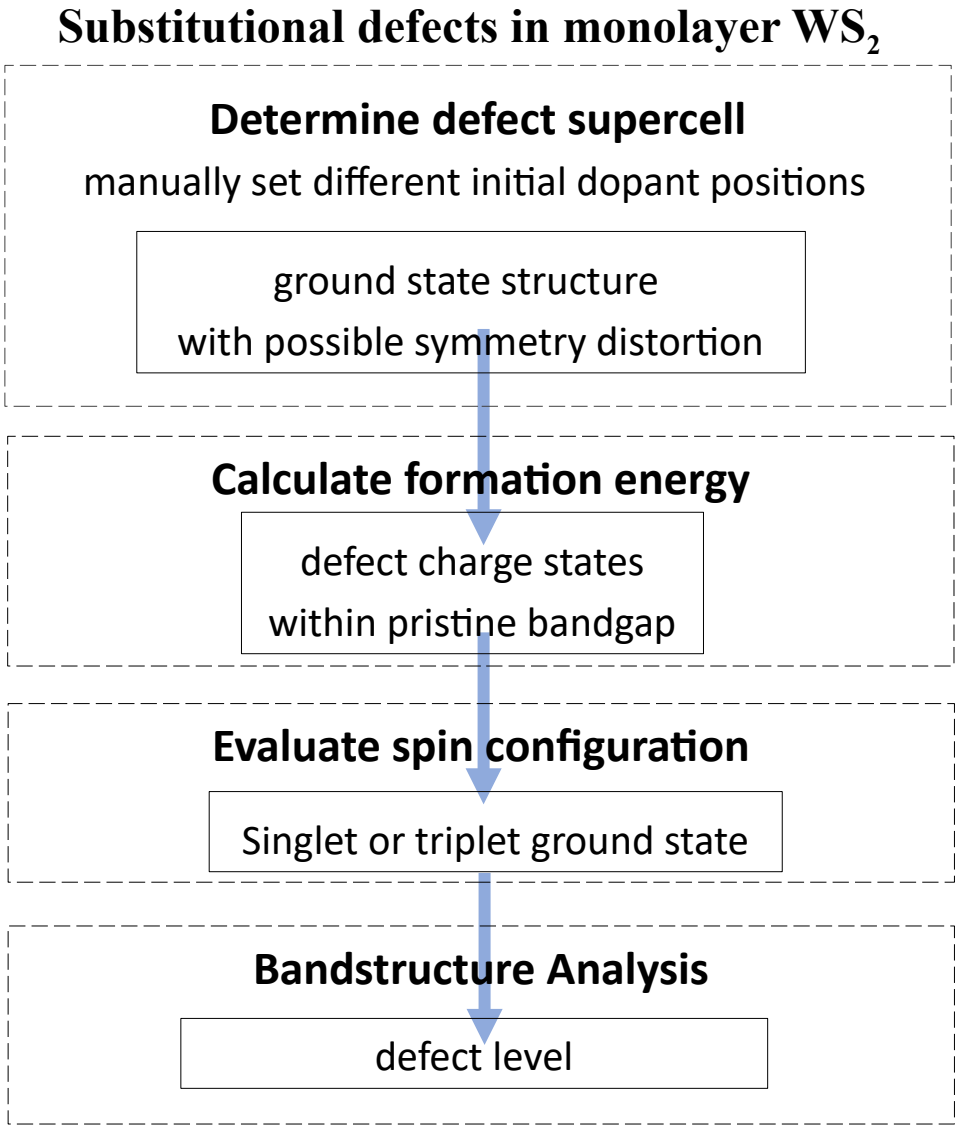
Workflow



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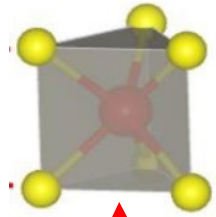
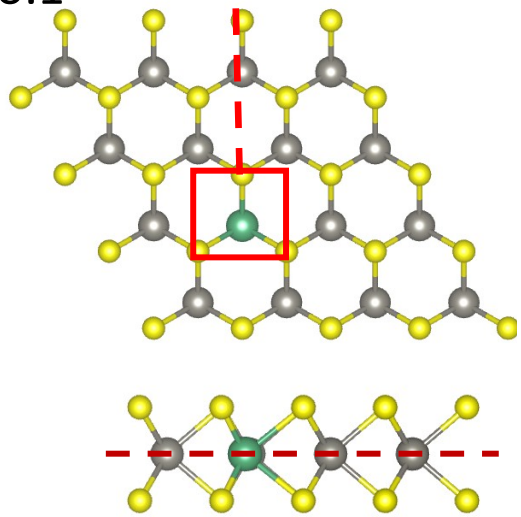
Defect Supercell

Initial Disruption Setting - relax the defect structures in symmetry broken supercells



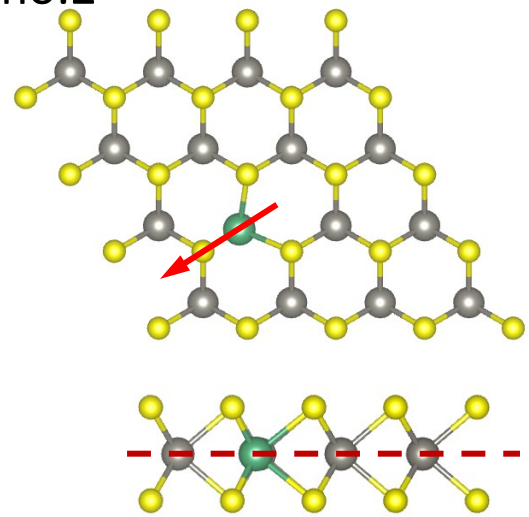
Trigonal prismatic coordination → $\mathbf{D_{3h}}$

no.1

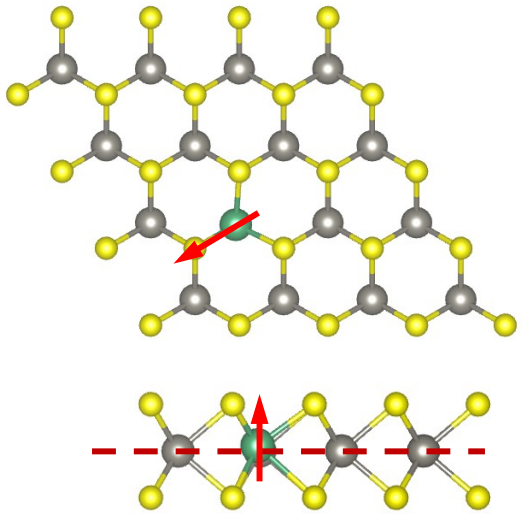


(0.333 0.417 0.500)

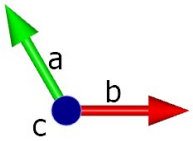
no.2



(0.305 0.405 0.500)



(0.320 0.410 0.505)



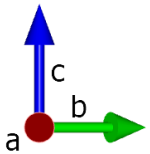


Fig.1 Top views and side views of the possible structures and symmetries

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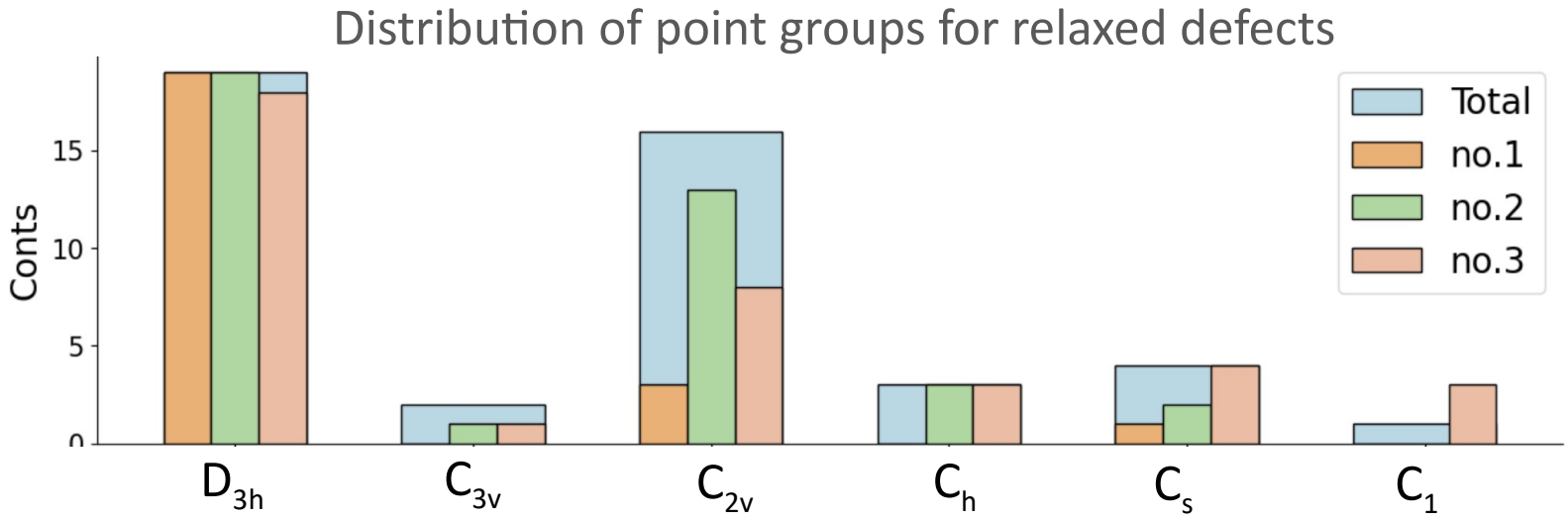
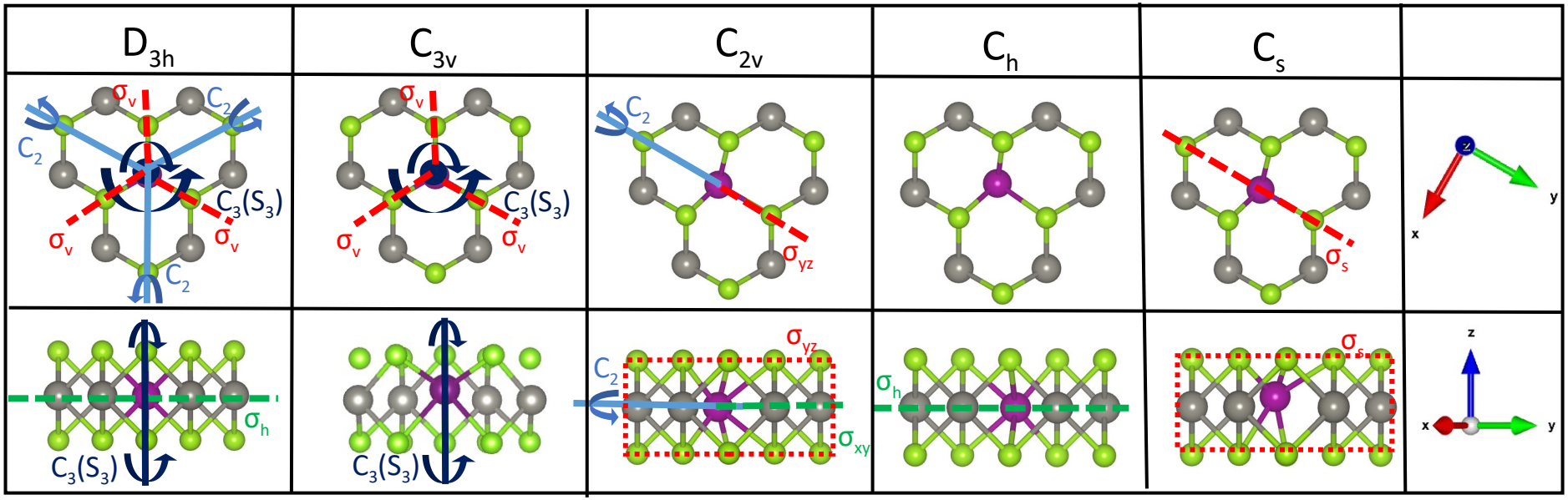
Defect Supercell





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Defect Formation Energy

$$\Delta H_{\mathrm{D,q}}(E_F,\mu) = [E_{\mathrm{D,q}} - E_{\mathrm{H}}] + \sum_i n_i\mu_i + qE_F + E_{\mathrm{corr}}$$

① ② ③ ④

Defect Formation Energy

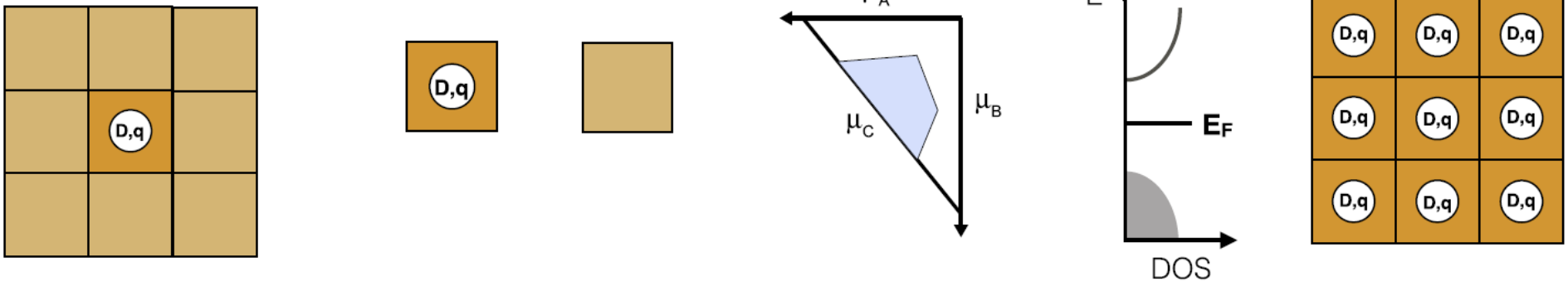
Defect Supercell

Host Supercell

Chemical potentials from phase stability

Electron chemical potential

Finite size corrections



Goyal, A. et al, *Comp. Mat. Sci.*, **2017**, *130*, 1-9

D = defect **q** = charge state **H** = host

$\mathbf{n_i}$ = number of atoms added to (negative) or removed from (positive) the host

$\boldsymbol{\mu_i}$ = chemical potential **i** = atomic species

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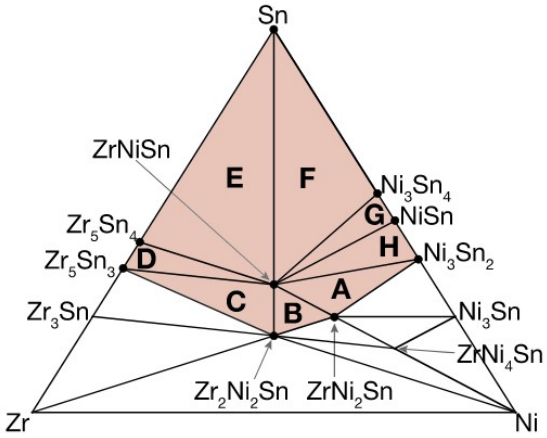
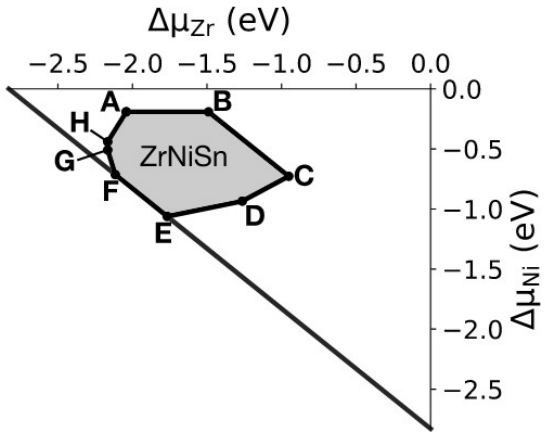
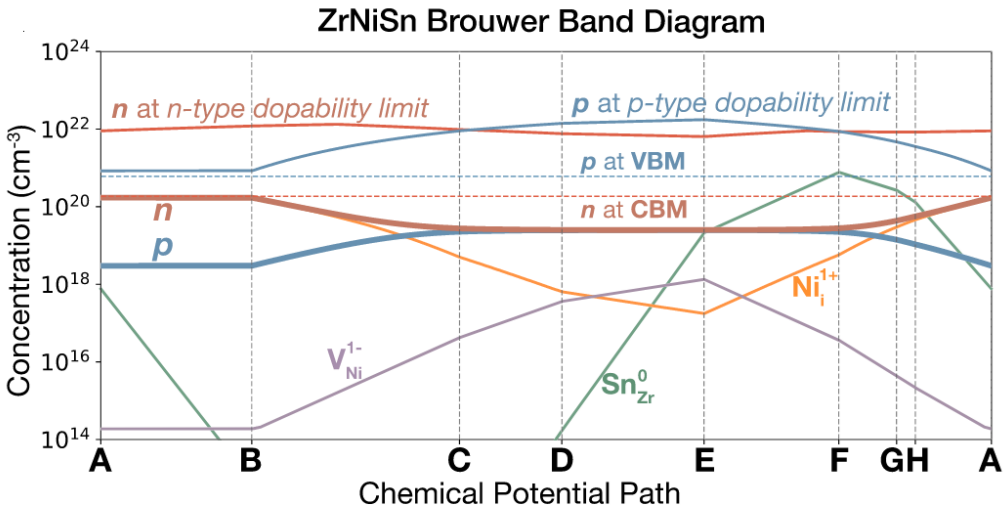
Chemical Potential Feasible Region & Limits



Fraction





Anand, S. et al. *Acc. Mater. Res.* **2022**, *3* (7), 685–696.

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Atom Chemical Potential

Constraints by phase stability:

$$\mu_W + 2\mu_S = E[\mathrm{WS_2}] \quad (1)$$

$$x\mu_{Nb} + y\mu_S \leq E[\mathrm{Nb}_x S_y] \quad (2)$$

$$\mu_W \leq E[\mathrm{W}] \quad (3)$$

$$\mu_S \leq E[\mathrm{S}] \quad (4)$$

$$\mu_{Nb} \leq E[\mathrm{Nb}] \quad (5)$$

$$\Delta\mu_A = \mu_A - \mu_A^0 \quad (6)$$

$$\mu_A^0 = E[A]$$

$$\Delta\mu_\mathrm{W} + 2\Delta\mu_\mathrm{S} = \Delta E[\mathrm{WS_2}] \quad (7)$$

$$x\Delta\mu_\mathrm{Nb} + y\Delta\mu_\mathrm{S} \leq \Delta E[\mathrm{Nb}_x S_y] \quad (8)$$

$$\Delta\mu_W \leq 0 \quad (9)$$

$$\Delta\mu_S \leq 0 \quad (10)$$

$$\Delta\mu_{Nb} \leq 0 \quad (11)$$

E[A]: energy per formula unit

$$\Delta E[\mathrm{A}_x\mathrm{B}_y] = E[\mathrm{A}_x\mathrm{B}_y] - xE[\mathrm{A}_x] - yE[\mathrm{B}_y] \quad (12)$$

μ_A^0 In electronic-structure calculations, chemical potentials can be referenced to the total energy of the elemental phases at T = 0 K.

ΔE
ΔH Energy enthalpy and formation energy are considered to have the same value since the pressure is small enough after relaxation.

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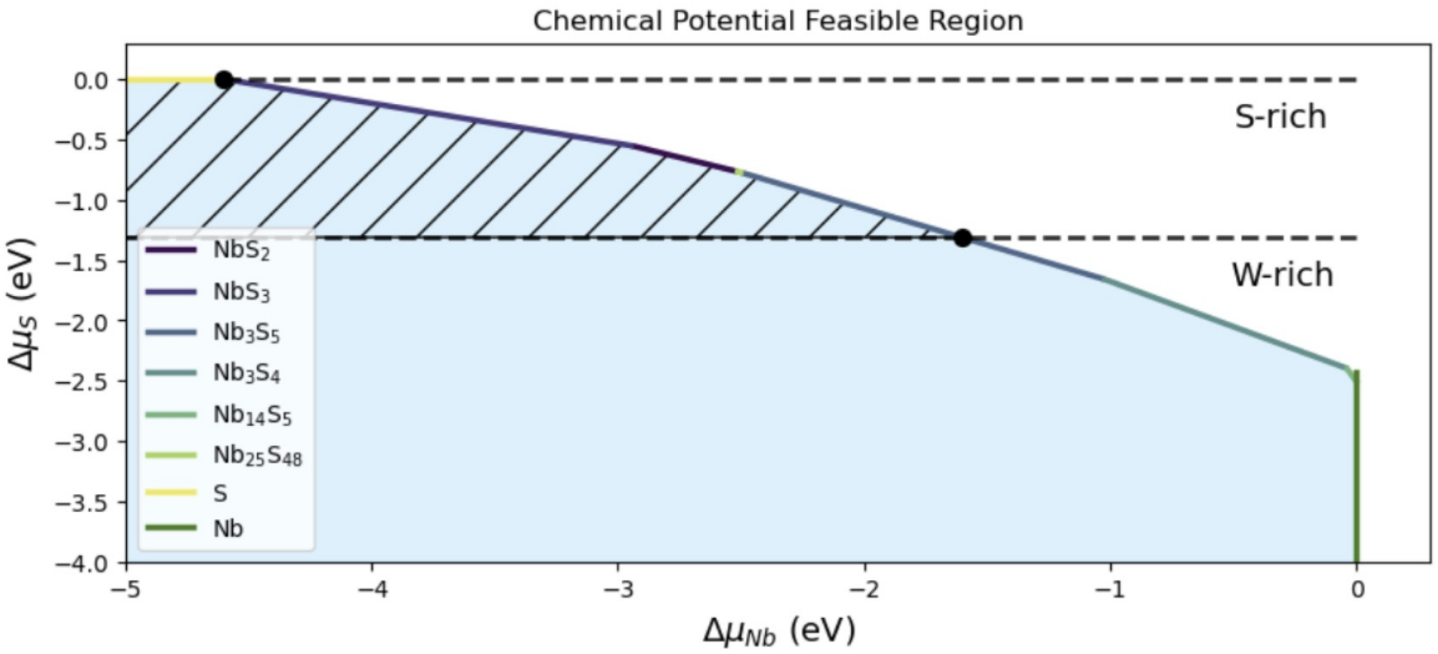
Atom Chemical Potential

As specifically corrected to fit experimental formation enthalpies, the formation enthalpy data from the Materials Project is implemented here to build constraints



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Charge Correction

Supercell approach: The isolated charged defect → periodically repeated array of defects → artificial electrostatic interactions

The FNV scheme: $\Delta E^{\mathrm{corr}} = E^{\mathrm{iso}}_{\mathrm{model}} - E^{\mathrm{periodic}}_{\mathrm{model}} + QC$

Image charge

- Determine the z-dependent dielectric function
- use a model charge distribution to emulate the behavior of the defect charge state, and find the model potential by solving the Poisson equation.

$$\rho(\mathbf{r}) = \frac{1}{\left(\sqrt{2\pi}\sigma\right)^3} e^{-\frac{(\mathbf{r}-\mathbf{r_0})^2}{2\sigma^2}}.$$

- Do it twice with periodic boundary conditions and zero boundary conditions. The electrostatic energy is given by:

$$U = \frac{1}{2}\int_{\Omega} \rho V$$

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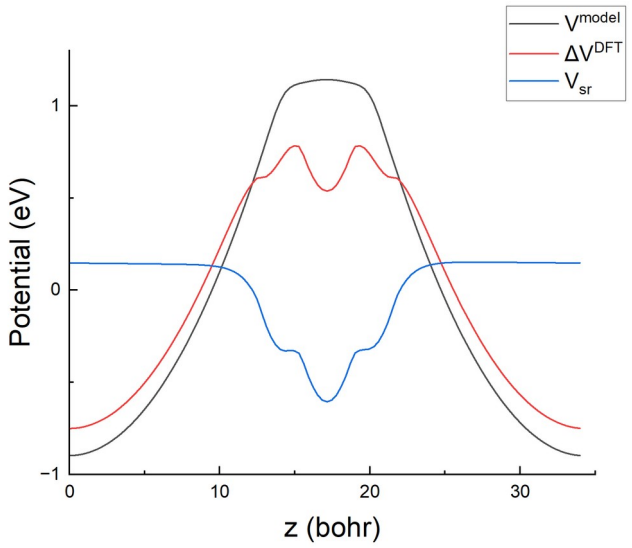
Charge Correction

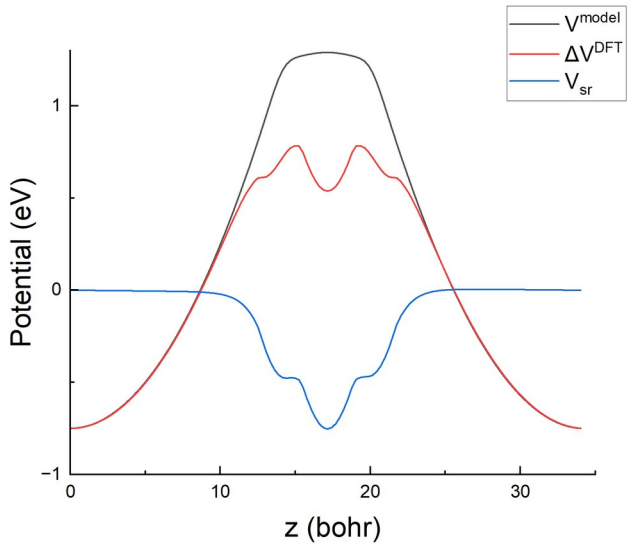
Potential alignment:

Manually set C until potential alignment:

$$\Delta \mathrm{V}^{\mathrm{DFT}} - \mathrm{V}^{\mathrm{model}} - \mathrm{C} \rightarrow 0$$ (away form defect)

Correction Energy: +1 : *0.094 eV* *-1 : 0.071 eV*





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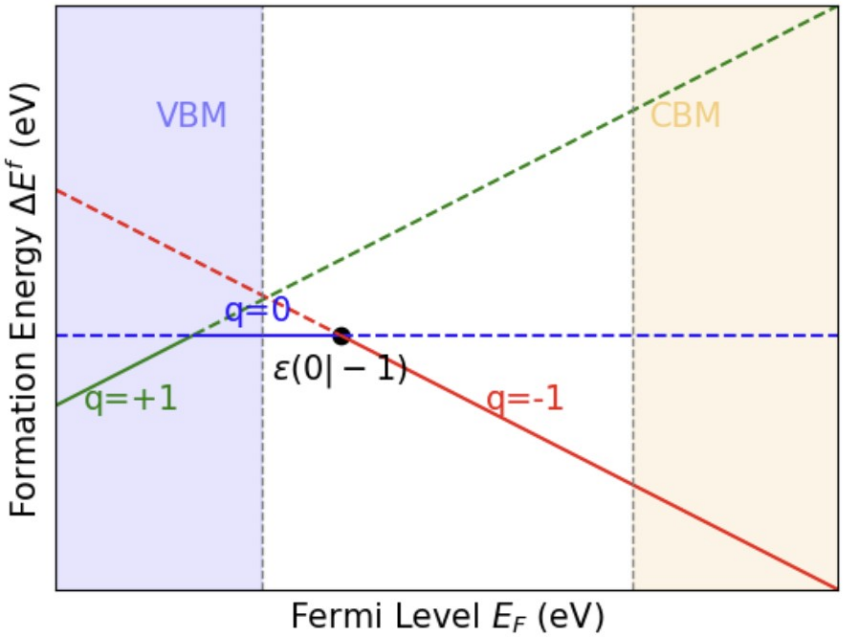
Formation Energy Diagram

Table 3 Formation energy values of charge states +1, 0, -1.

Defect	*q*	$E_{D,q} - E_{Host}$	qE_{VBM}	$\Sigma n_i\mu_i$ *(S-rch/Wrich)*	E_{corr}	$Ef(E_F=VBM)$ *(S-rch/W-rich)*
Nb_W^{+1}	+1	4.076	-1.518	-2.001/-1.675	0.094	0.651/0,977
Nb_W^{0}	0	2.232	0	-2.001/-1.675	0	0.231/0.557
Nb_W^{-1}	-1	1.098	1.518	-2.001/-1.675	0.071	0.686/1.012

$$\sum n_i\mu_i = 1\Delta\mu_W - 1\Delta\mu_{Nb} =$$
$$= (\Delta\mu_W + \mu_W^0) - (\Delta\mu_{Nb} + \mu_{Nb}^0)$$
$$= \begin{cases} -2.001\text{eV} & \text{S rich} \\ -1.675\text{eV} & \text{W rich} \end{cases}$$



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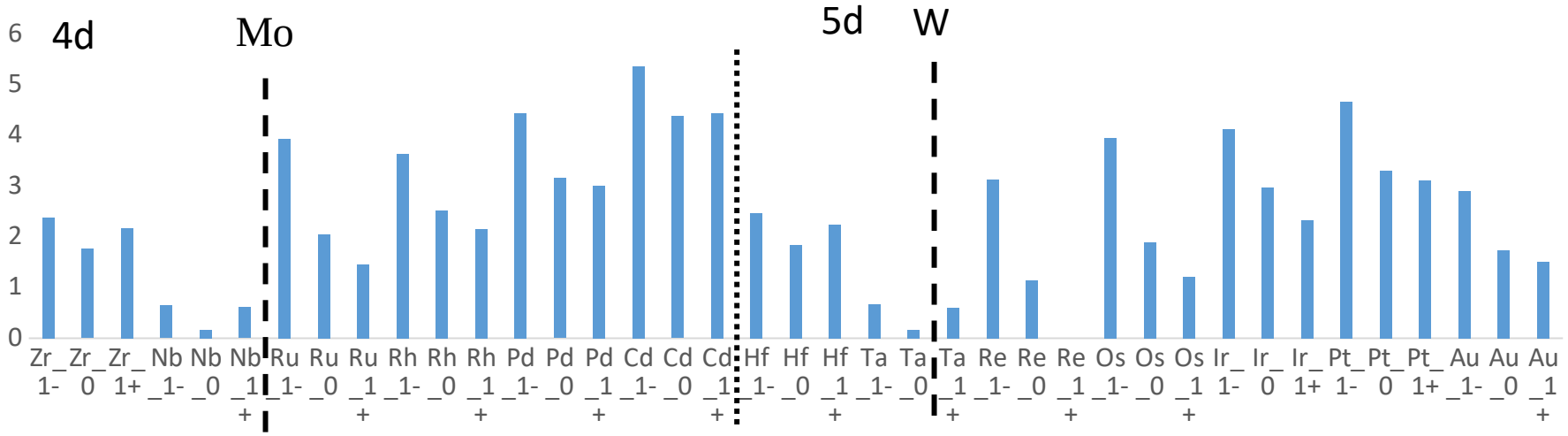
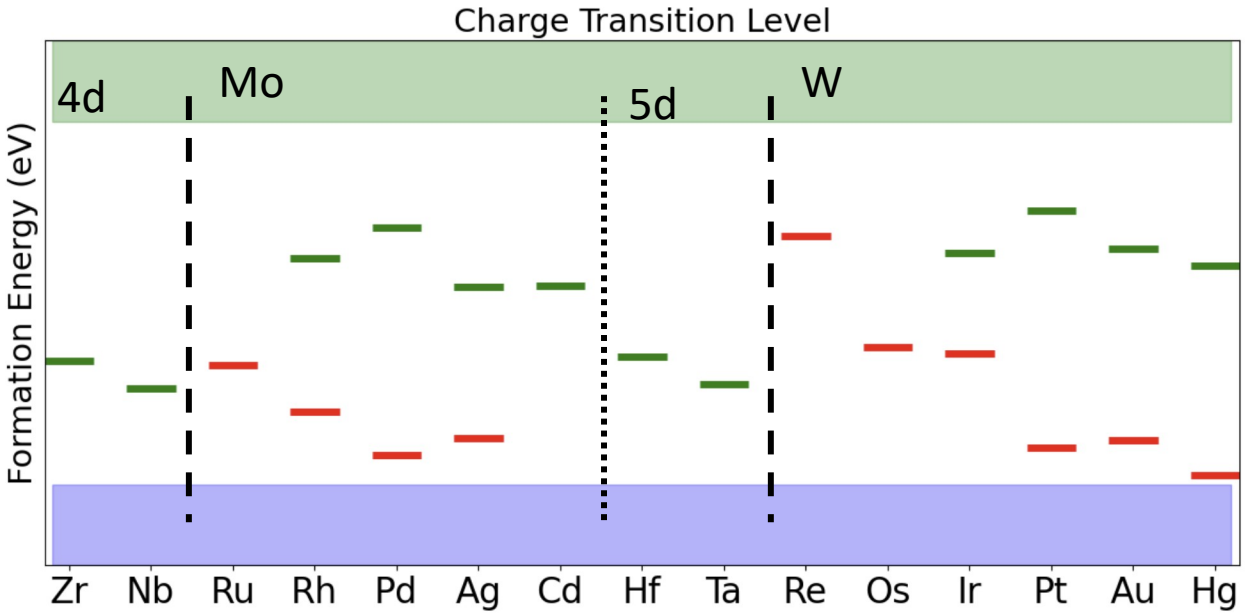
Charge Transition Level





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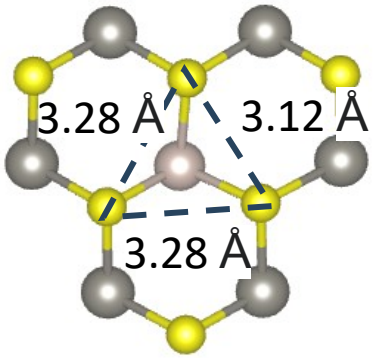
Spin Configuration

TM Defect	Charged state	Symmetry	(Singlet-Triplet)(eV)
Rh	+1		0.06
Hg	0		0.04
	0		0.03
	-1		-0.05
…	…		…

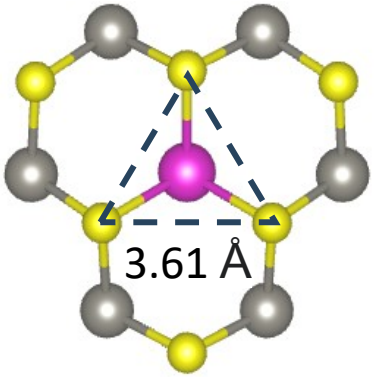
In-plane strain for triplet ground state structure:

Rh^{1+}



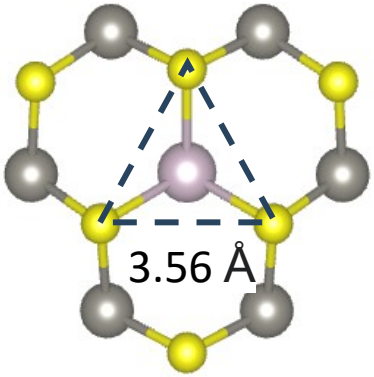
C_S

Hg^0



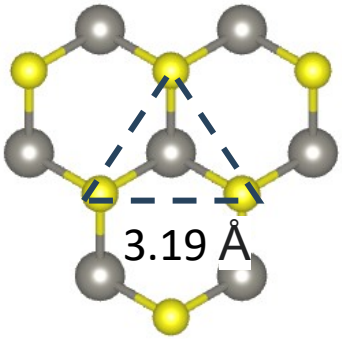
D_{3h}

Cd^0



D_{3h}

Pristine



D_{3h}

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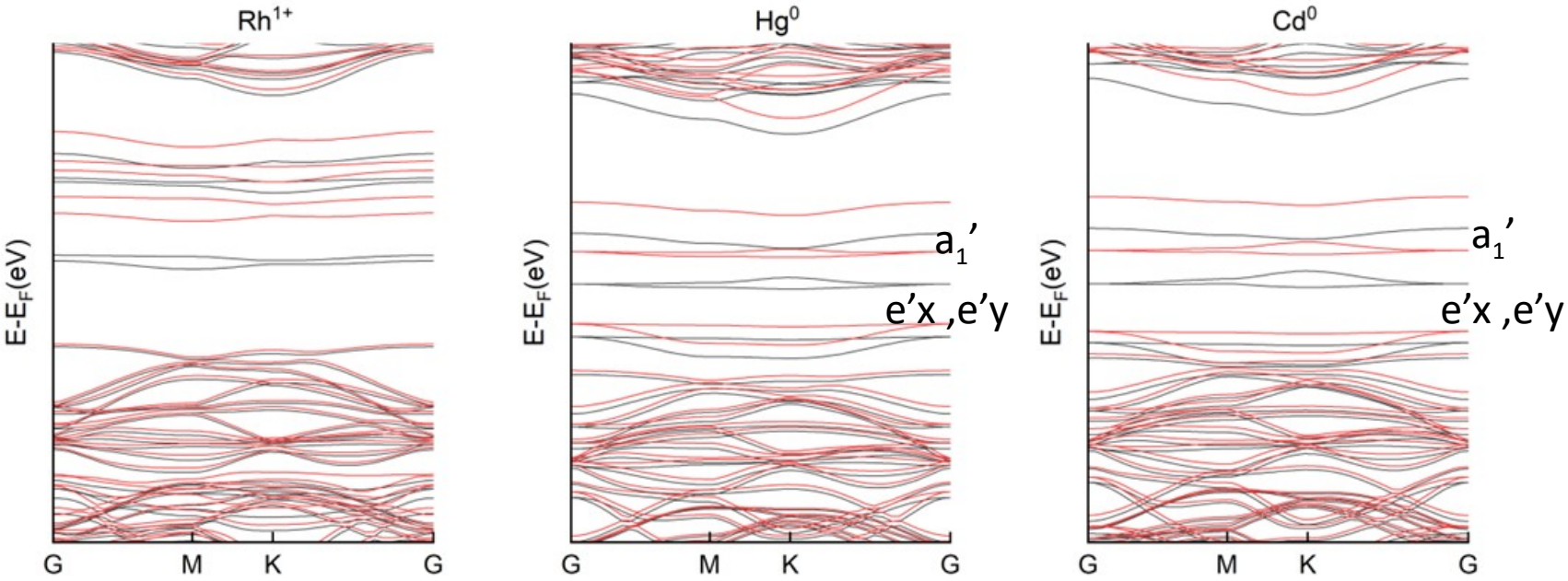
Bandstructure



Calculated band structure of triplet ground state defects

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