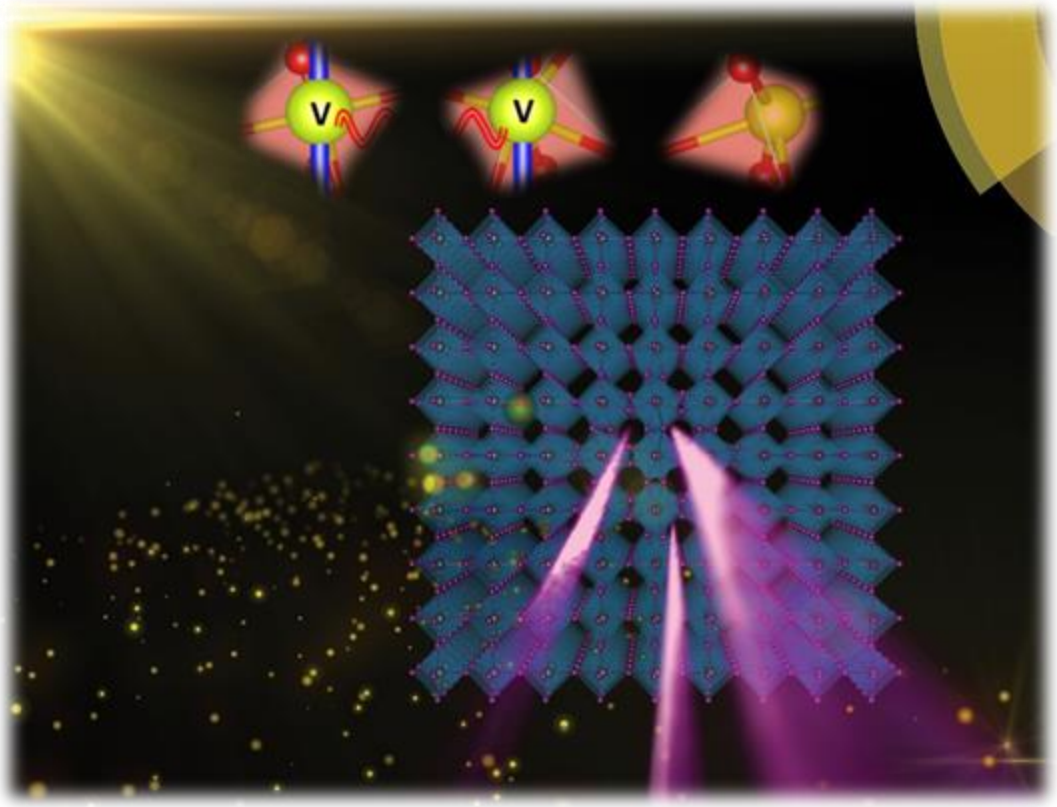
DFT applications in Physics and Chemistry and their technical aspects



Byungkyun Kang

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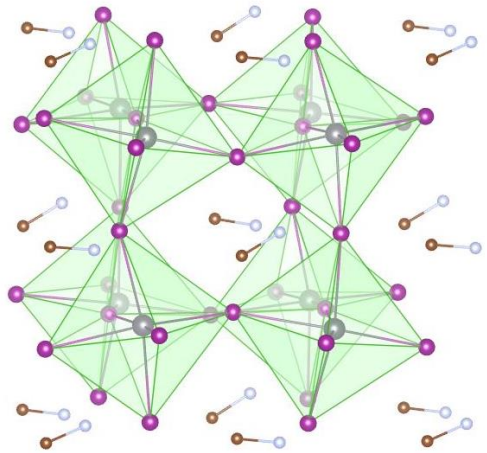
Computational Materials Physics Bootcamp at UD August 2024

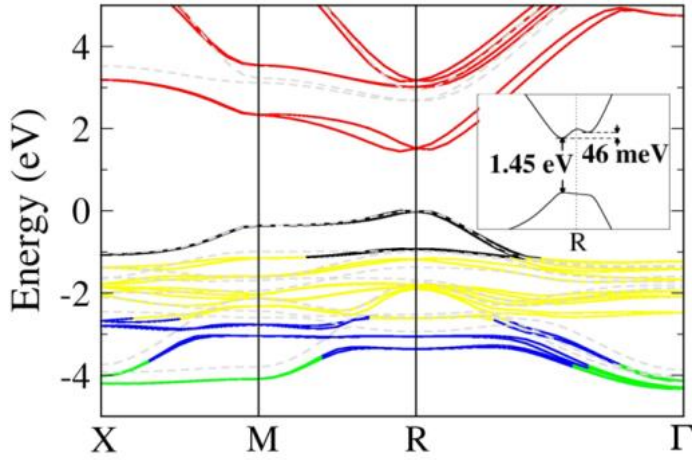
Goal

- Broaden DFT applications in Physics and Chemistry
- Methods dependent.

First-Principles Methods for real materials

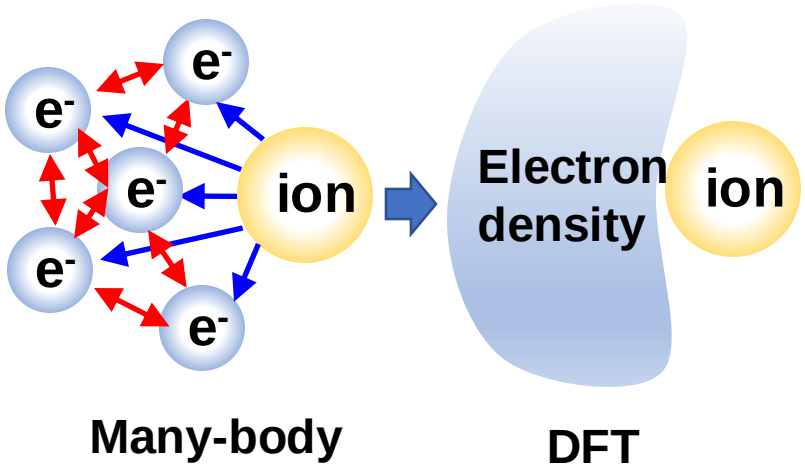
- Density functional theory
- No empirical parameter
- Incorporating rapidly growing computer power





Material + Computer ➡ Physics

Density Functional Theory



- DFT solve electronic structure from first-principles
- Ground state is unique with self-consistent
- W. Kohn 1999 Nobel Prize for chemistry.

DFT+U (hybrid functional) for strong correlation

- Add electron correlation U on static mean-field
- Work for magnetic ground state
- Practical for supercell

[1] P. Hohenberg, W. Kohn, Phys. Rev. B 136, 864 (1964).
[2] W. Kohn, L. J. Sham, Phys. Rev. B 140, 1133 (1965).

Density Functional Theory Packages

molecular code vs. a periodic code

local orbital vs. plane wave as basis set

all electron vs. pseudo potential

https://dft.sandia.gov/dft-codes-and-web-sites/

Periodic codes (principally)

Local orbital basis codes

- QUEST: SeqQuest – gaussian basis pseudopotential code
- SIESTA – numerical atom-centered basis pseudopotential code
- CRYSTAL – CSE – gaussian basis all-electron code
- AIMPRO
- FHI-AIMS – (commercial license) full potential, all-electron, numerical or
- FPLO
- OpenMX – GPL – numerical atom-centered basis PP code (Ozaki group)

All-electron (augmented methods) codes

- ELK – GPL – FP-LAPW
  (one branch from the old EXCITING code)
- EXCITING – FP-LAPW, focus on excited state properties (TDDFT, MBPT)
  [license not apparent on website, probably open source]
  (another branch from the old EXCITING code)
- FLEUR – "freely available" – FLAPW code
- RSPt – "Open Source" – FP-LMTO
- WIEN2k – modest fee – full potential LAPW

Density Functional Theory Packages

Periodic codes (principally)

Plane wave and related (real space, wavelet, etc.) methods

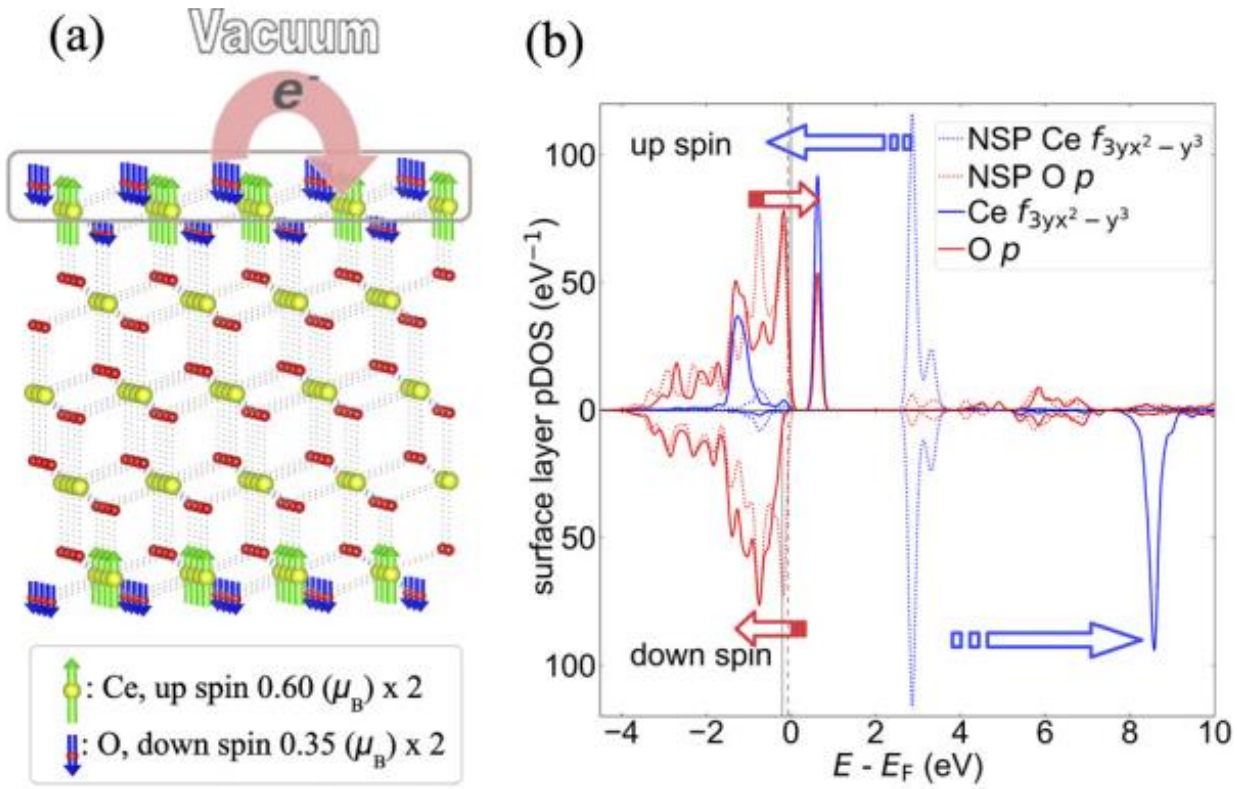
- VASP
- CASTEP
- CPMD
- ABINIT – GPL
- BigDFT – GPL – wavelets
- Quantum-Espresso (formerly PWscf) – GPL
- PEtot – GPL
- DACAPO – GPL
- Socorro – GPL
- JDFTx formerly known as DFT++ – GPL
- Paratec
- PARSEC – GPL – real space, pseudopotential
- CP2K – GPL (mixed basis DFT)
- GPAW – GPL – real-space multigrid PAW code
- SPHINX
- QBOX – GPL – plane wave pseudopotential, large parallel

Molecular codes (principally)

- Gaussian.com
- NWChem
- O c topus – GPL – real space TDDFT code
- DMol^3 – Accelrys Materials Studio
- Jaguar – Schrodinger, Inc.
- GAMESS
- QCHEM
- NRLMOL
- MondoSCF (no license info, but appears “free”)
- ADF – SCM
- deMon
- CADPAC – The Cambridge Analytic Derivatives Package
- PYQUANTE – GPL – python-based development toolset for DFT/HF
- TURBOMOLE – DFT and HF for large molecular systems

Modeling surface spin polarization on ceria-supported Pt nanoparticles – CP2K

Geometry Optimization with Magnetic

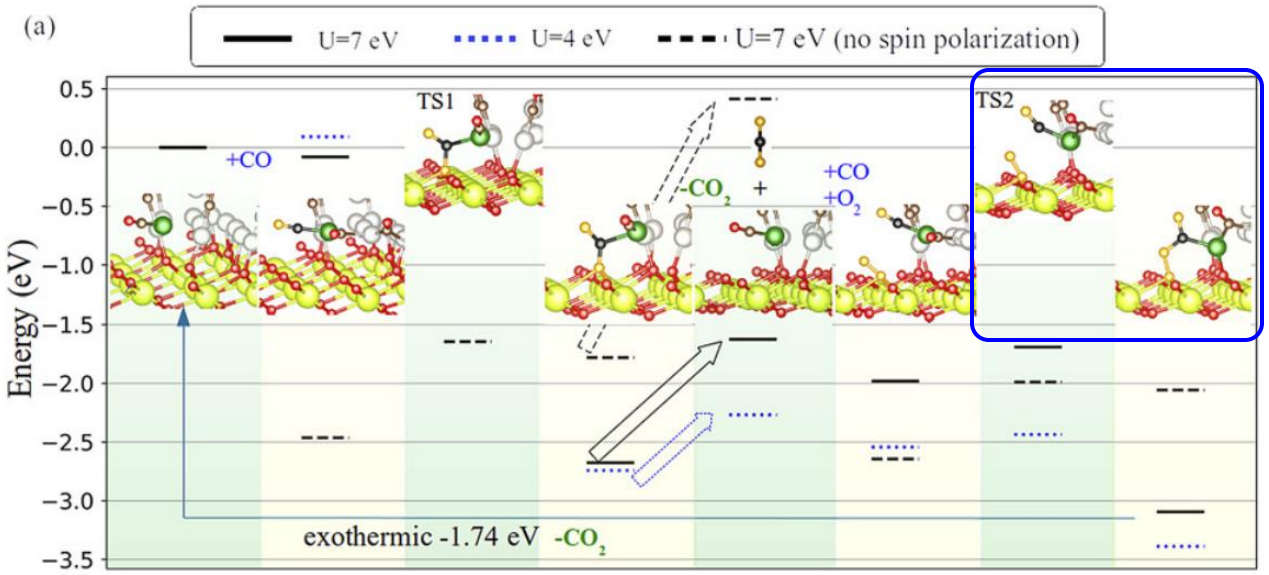


- Construct O terminated supercell with enough vacuum
- Set U in DFT+U
- Set initial spin configuration

```
&SUBSYS
  &CELL
    ABC 22.95150 22.95150 43.23521
    ALPHA_BETA_GAMMA 60. 60. 60.
    PERIODIC XYZ
&END CELL
  &COORD
   SCALED
Ce -1.601952882845925e-09 4.805241177185948e-09 0.08847534163779093
Ce -3.203905737936275e-09 9.610482284982957e-09 0.1769506823023531
...
O 0.8749999899877952 0.8750000300327559 0.5529708613920896
O 0.8749999883858415 0.8750000348379988 0.6414462312535135
  &END COORD
 &KIND Pt
    MAGNETIZATION     5.0000000000000000E-01
    BASIS_SET DZVP-MOLOPT-SR-GTH-q18
    POTENTIAL GTH-PBE-q18
  &END KIND
  &KIND O
    BASIS_SET DZVP-GTH-PBE
    POTENTIAL GTH-PBE-q6
  &END KIND
&KIND Ce
    MAGNETIZATION     5.0000000000000000E-01
    BASIS_SET DZVP-MOLOPT-SR-GTH-q12
    POTENTIAL GTH-PBE-q12
    &DFT_PLUS_U
     L 3
     U_MINUS_J [eV] 7.0
    &END DFT_PLUS_U
  &END KIND
 &END SUBSYS
```

[1] **B. Kang**, et al., J.Phys.Condens.Matter. 34 255002 (2022).

Nudged elastic band method (NEB)

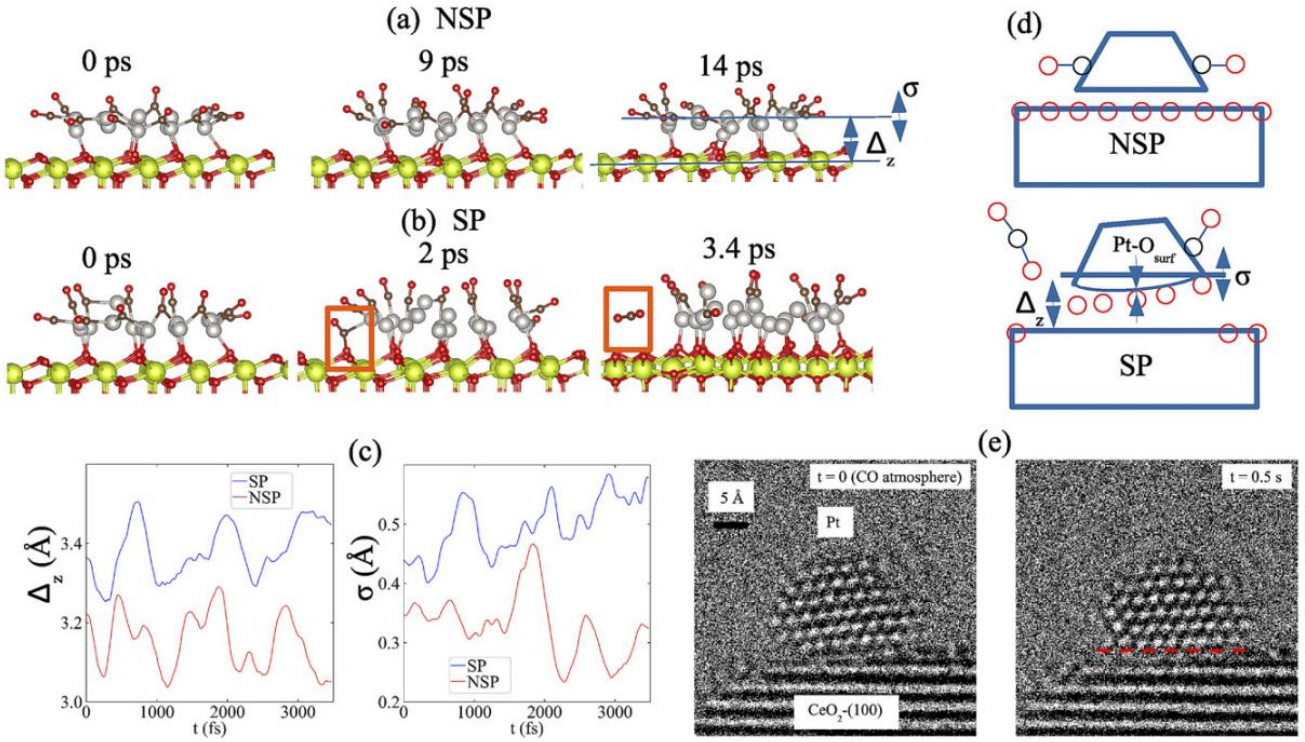


- Energy profiles for reaction pathway for CO oxidation on Pt/Co on ceria support
- MvK mechanism: $CO+O_{suf}$ -> $-CO_2+O_{vac}$; O_2 at O_{vac}; CO+one O (from O_2) -> $-CO_2$
- Set number of images
- Find activation barrier

```
&MOTION
 &BAND
  NUMBER_OF_REPLICA 10          # Number of "replica" geometries along the path
  K_SPRING 0.05
  &OPTIMIZE_BAND
   OPT_TYPE DIIS
   &DIIS
    MAX_STEPS 1000
   &END
  &END
  BAND_TYPE CI-NEB              # Climbing-image NEB
  &CI_NEB
   NSTEPS_IT  5                 # First take 5 normal steps, then start CI
  &END
  &REPLICA
   COORD_FILE_NAME init.xyz
  &END
  &REPLICA
   COORD_FILE_NAME final.xyz
  &END
  &PROGRAM_RUN_INFO
   INITIAL_CONFIGURATION_INFO
  &END
 &END BAND
&END MOTION
```

[1] **B. Kang**, et al., J.Phys.Condens.Matter. 34 255002 (2022).

Ab initio molecular dynamic simulations

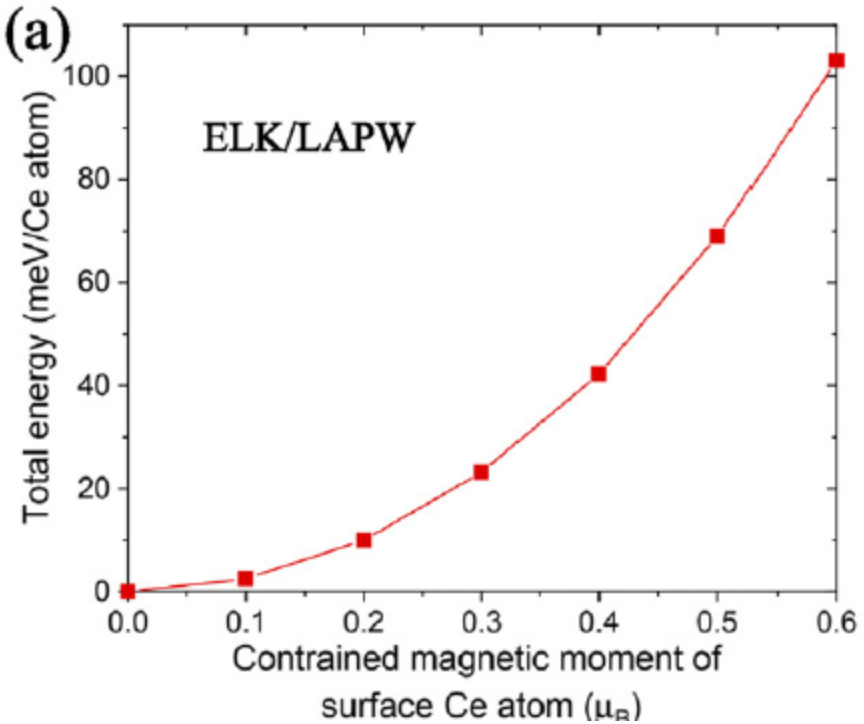


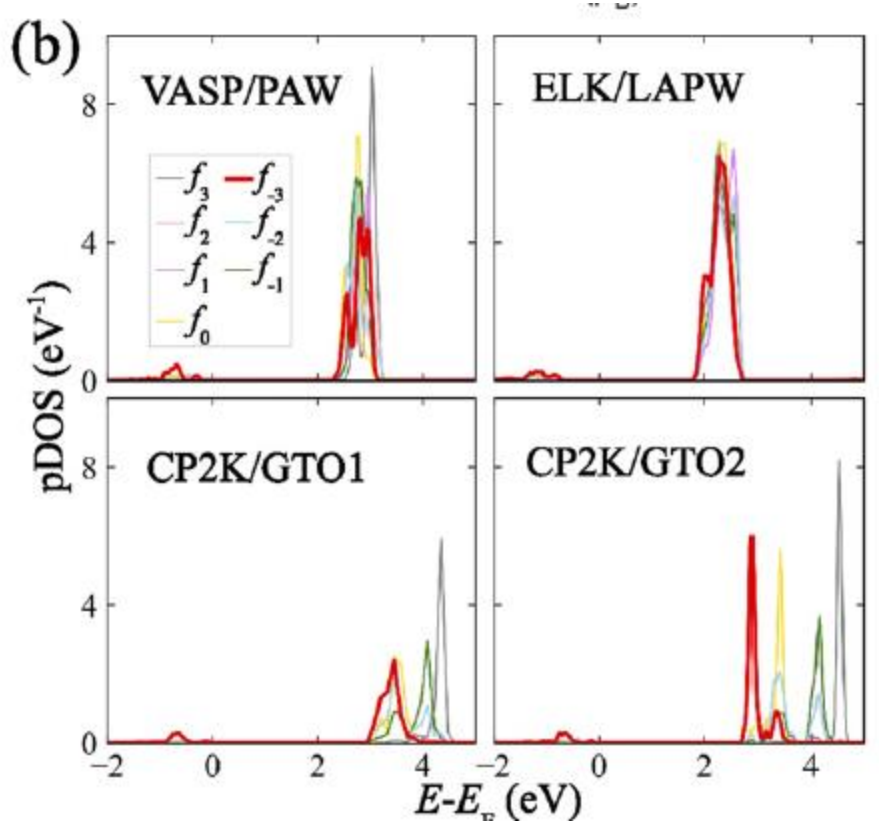
- Set temperature, time step, etc.
- ~1000 atoms geometry optimization on HPC
- ~500 atoms ab-initio MD on HPC
- Electron microscopy data show dynamic structural change taking place in a CO atmosphere
- Surface ferromagnetism (SP) MD explain experiments

```
&MD
 ENSEMBLE NVT  ! sampling the canonical ensemble, accurate properties might need NVE
 TEMPERATURE [K] 300
 TIMESTEP [fs] 1.0
 STEPS 30000
&THERMOSTAT
 &NOSE                #Uses the Nose-Hoover thermostat
   TIMECON 4          #timeconstant of the thermostat chainyour system
  &END NOSE
 &END THERMOSTAT
&END
 &PRINT
  &TRAJECTORY
   &EACH
    MD 1
   &END EACH
  &RESTART_HISTORY
   &EACH
    MD 500
   &END EACH
  &END RESTART_HISTORY
&RESTART
   BACKUP_COPIES 3
&END RESTART
 &END PRINT
 &CONSTRAINT
  &FIXED_ATOMS
   COMPONENTS_TO_FIX XYZ
   LIST 222 219 216 213 210 207 204 201 198 195 192 189 187 184 181 178 175 172 169
166 163 160 157 154 151 148 145 142 139 136 133 130 127 124 121 118 115 112 109 106
103 100 97 94 91 88 85 82 79 76 73 70 67 64 61 58 55 52 49 46 43 40 37 34 31 28 25 22
19 16 13 10 7 4 1
  &END
 &END
```

[1] **B. Kang**, et al., J.Phys.Condens.Matter. 34 255002 (2022).

Cross-validation of the DFT simulation results - CP2K, ELK, VASP





- ELK with fixed spin moments on surface Ce lead to increased total energy.
- Electron localization is more pronounced for GTO2 than GTO1, PAW, and LAPW.
- Only GTO2 (more confined Gaussian basis) give rise to the surface spin polarization.
- Stable surface spin polarization depend on choice of basis set.

[1] **B. Kang**, et al., J.Phys.Condens.Matter. 34 255002 (2022).

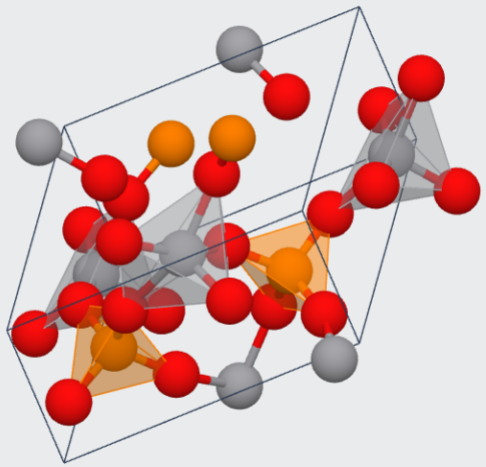
Spin-spin interaction in ε-$VOPO_4$ through doping light elements – VASP

Use Materials Project

VPO_5 mp-556459

Show Help Guides

Electronic Structure | X-Ray Diffraction | X-Ray Absorption | Substrates | Similar Structures | Calculation Summary | Provenance/Citation



O P V Atoms Unit Cell Bonds Polyhedra CIF

Zoom in/out — Shift + Drag cursor
Rotate along the center axis — Option + Drag cursor

Edit Crystal | Generate Phase Diagram

Tags: Oxovanadium(V) phosphate(V) - epsilon

File Formats | 1 file(s)

Material Details

Final Magnetic Moment
0.000 μ_B

Magnetic Ordering
NM

Formation Energy / Atom
-2.506 eV

Energy Above Hull / Atom
0.003 eV

Density
3.10 g/cm^3

Decomposes To
VPO_5

Band Gap
1.947 eV

Space Group

Hermann Mauguin
Cc [9]

Hall
C 2yc

Point Group
m

Crystal System
monoclinic

Lattice Parameters

a	5.096 Å	α	72.072°
b	5.096 Å	β	72.072°
c	7.389 Å	γ	87.728°

Volume 173.392 Å^3

Final Structure

Fractional Coordinates — CIF

V

a	b	c
0.2309	0.7693	0.5048
0.7693	0.2309	0.0047

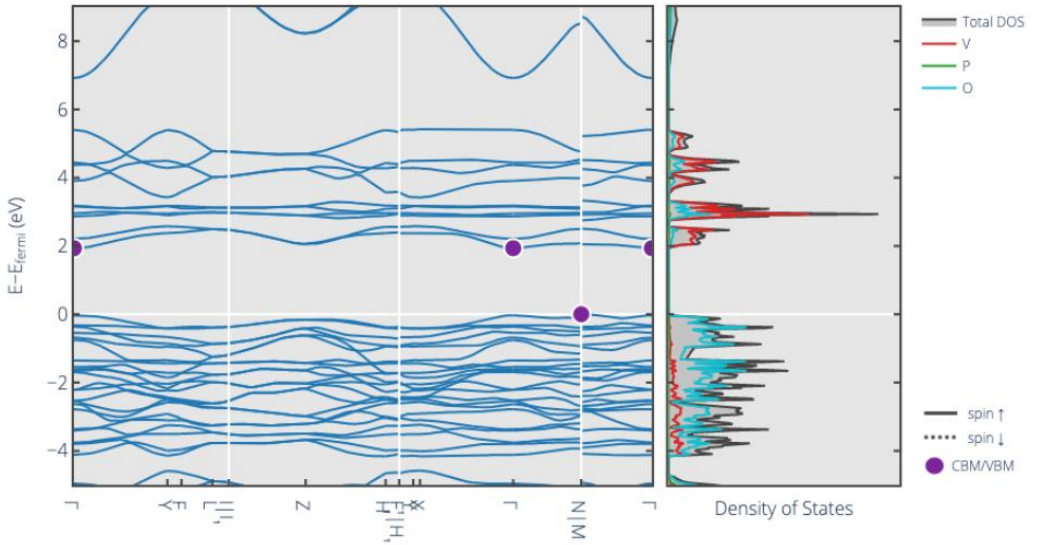
P

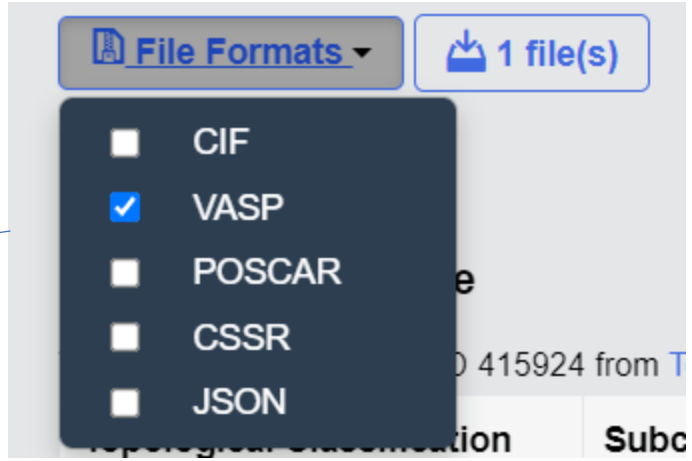
a	b	c
0.1692	0.4118	0.2158
0.4118	0.1692	0.7158

O

a	b	c
0.1267	0.1298	0.3803
0.1298	0.1267	0.8803
0.1481	0.6514	0.3038
0.4408	0.4565	0.5533
0.4445	0.9427	0.613

Band Structure and Density of States





Four Input files

POSCAR

```
V4 P4 O20
1.0
6.645076 0.000000 -3.137366
0.000000 7.062710 0.000000
0.000000 0.000000 7.389046
V P O
4 4 20
direct
0.999892 0.230840 0.004750 V
0.999892 0.769161 0.504750 V
0.499893 0.730839 0.004750 V
0.499893 0.269161 0.504750 V
0.209506 0.378723 0.715829 P
0.209506 0.621278 0.215829 P
0.709506 0.878722 0.715829 P
...
0.600224 0.748344 0.803829 O
0.306417 0.249121 0.613017 O
0.871717 0.998462 0.880282 O
0.306417 0.750879 0.113017 O
0.551332 0.007827 0.553260 O
0.551332 0.992173 0.053260 O
0.191911 0.150589 0.195233 O
```

KPOINTS

```
pymatgen with grid density = 1282 / number of atoms
0
Gamma
3 3 3
```

POTCAR.spec

```
V_pv
P
O
```

INCAR

```
ALGO = Fast
EDIFF = 0.0014
ENCUT = 520
IBRION = 2
ISIF = 3
ISMEAR = -5
ISPIN = 2
LASPH = True
LDAU = True
LDAUJ = 0 0 0
LDAUL = 2 0 0
LDAUPRINT = 1
LDAUTYPE = 2
LDAUU = 3.25 0 0
LMAXMIX = 4
LORBIT = 11
LREAL = Auto
LWAVE = False
MAGMOM = 4*5.0 24*0.6
NELM = 100
NSW = 99
PREC = Accurate
SIGMA = 0.05
```

DFT+U spin polarized simulation

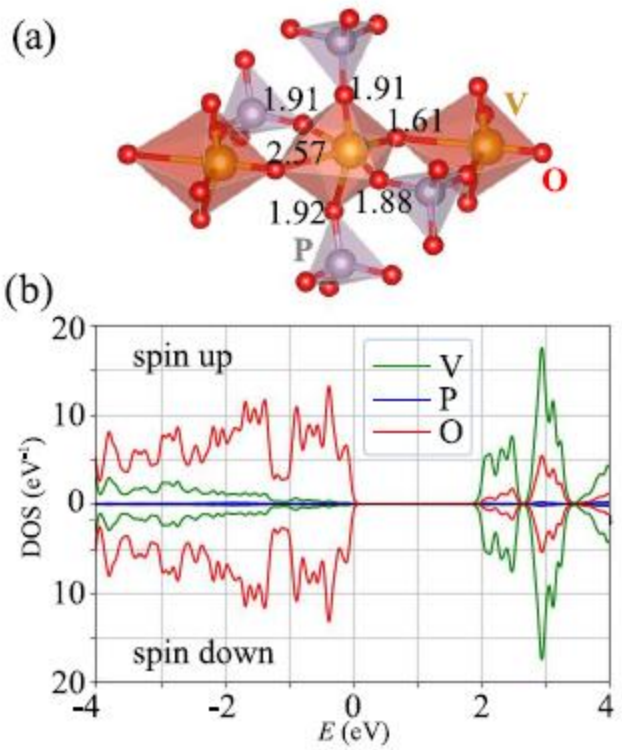


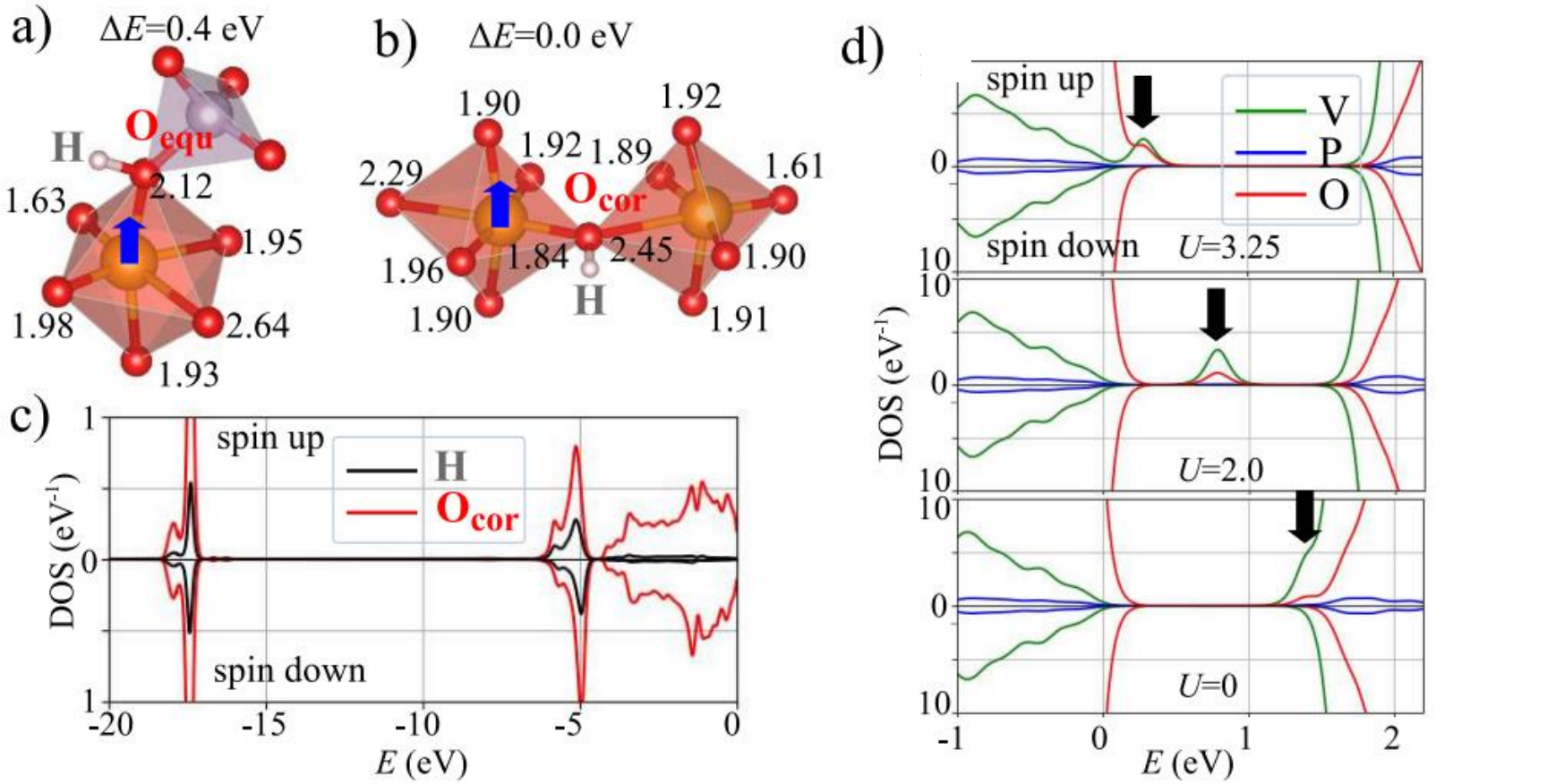
Figure 1. (a) Optimized structure of the VO_6 octahedron in ε-$VOPO_4$. The bond lengths of V–O are presented in units of Å. (b) Spin-polarized atom-projected density of states. The valance band maximum is set to zero.

- Spin polarized DFT+U
- No magnetization

```
ALGO = Fast
EDIFF = 0.0014
ENCUT = 520
IBRION = 2
ISIF = 3
ISMEAR = -5
ISPIN = 2
LASPH = True
LDAU = True
LDAUJ = 0 0 0
LDAUL = 2 0 0
LDAUPRINT = 1
LDAUTYPE = 2
LDAUU = 3.25 0 0
LMAXMIX = 4
LORBIT = 11
LREAL = Auto
LWAVE = False
MAGMOM = 4*5.0 24*0.6
NELM = 100
NSW = 99
PREC = Accurate
SIGMA = 0.05
```

[1] **B. Kang**, and Q. Zhu, (2022) under review in J.Phys.Chem.C

Electron localization by H doping and U effect.

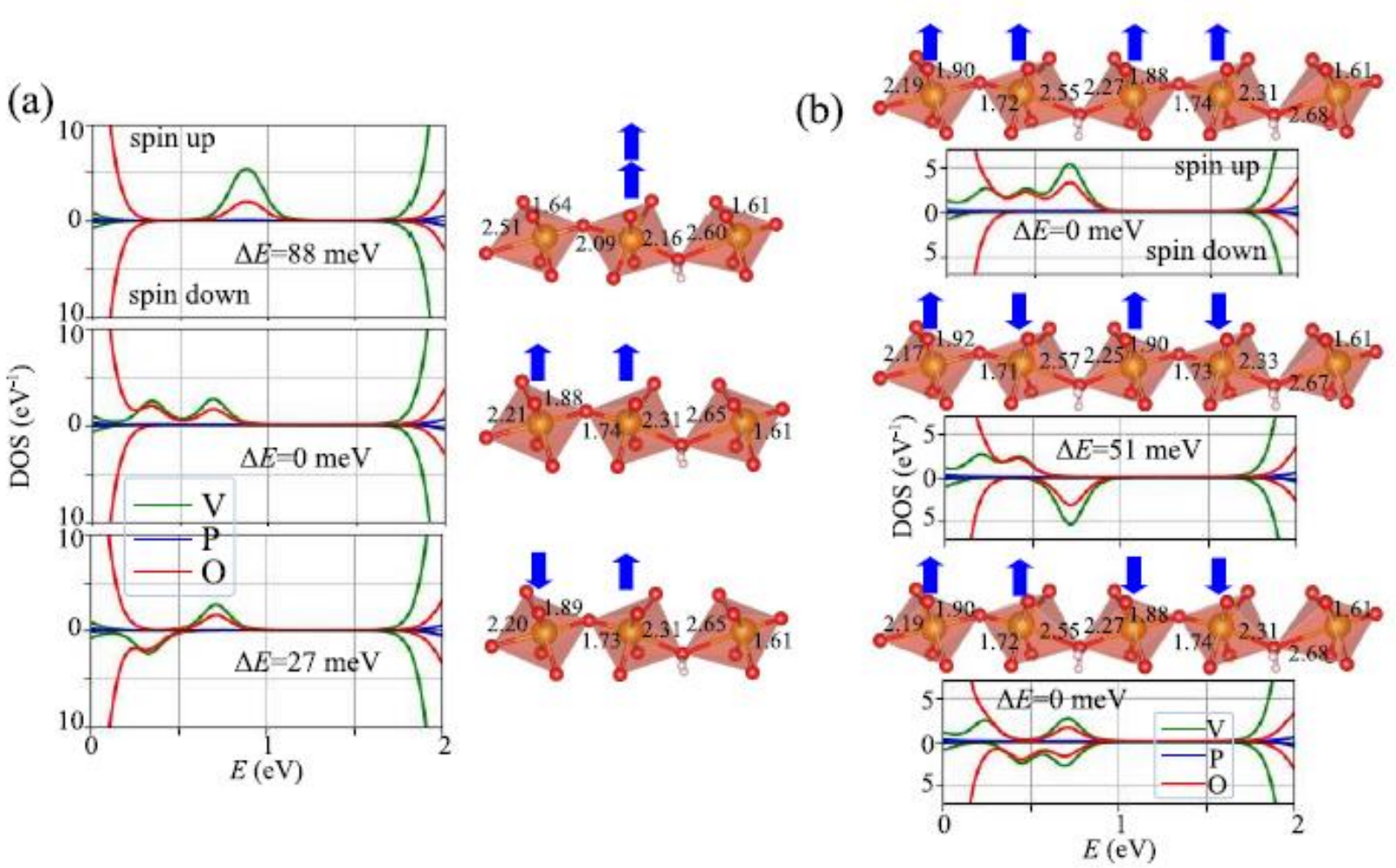


Set valance band max zero (not Ef)

- Find H defect configuration.
- H at corner oxygen is more stable
- O_{cor}-H bond leads to a charge transfer from O_{cor} to V
- Transferred charge is localized on V with spin momentum
- Sufficient U > 2.0 eV is necessary to localize the electron on V-d

[1] **B. Kang**, and Q. Zhu, (2022) under review in J.Phys.Chem.C

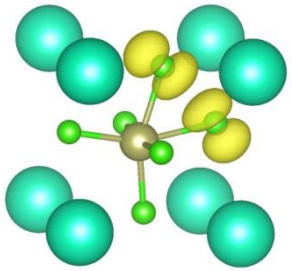
Spin-spin interaction in ε-$VOPO_4$ through doping light elements



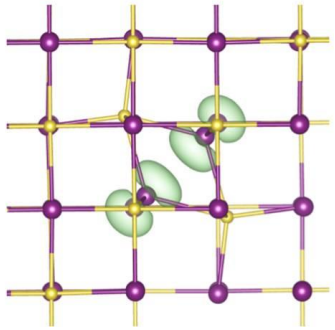
- With doping of H gas, ferromagnetic ordering is stable.

[1] **B. Kang**, and Q. Zhu, (2022) under review in J.Phys.Chem.C

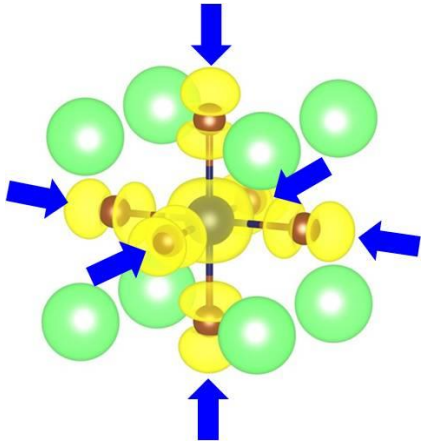
Small polarons using Hybrid functional – VASP



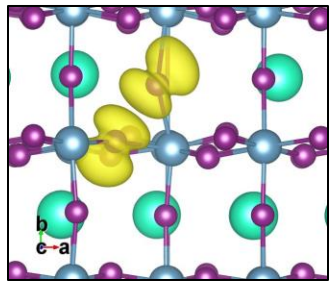
Cs_2HfCl_6
Binding E=0.71 eV



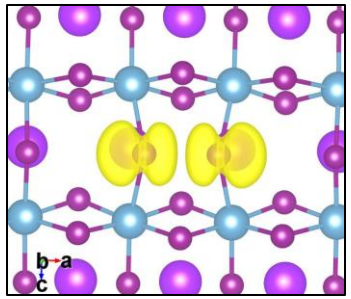
NaI
BE=0.19 eV



Cs_4PbBr_6
BE=0.09 eV

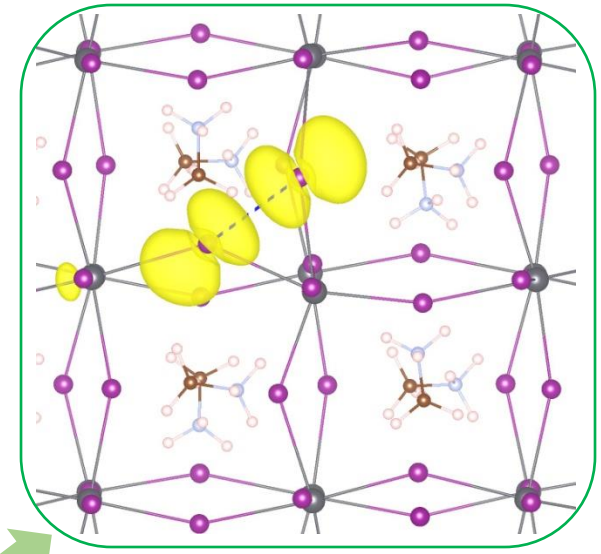


$CsCaI_3$
BE=0.16 eV

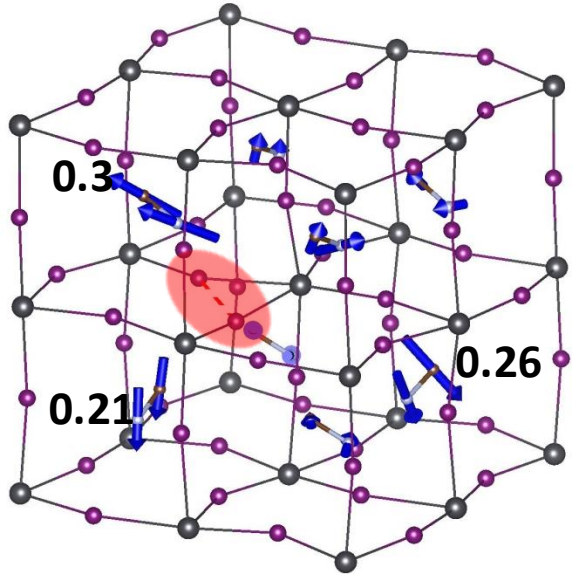


$KCaI_3$
BE=0.07 eV

$CH_3NH_3PbI_3$



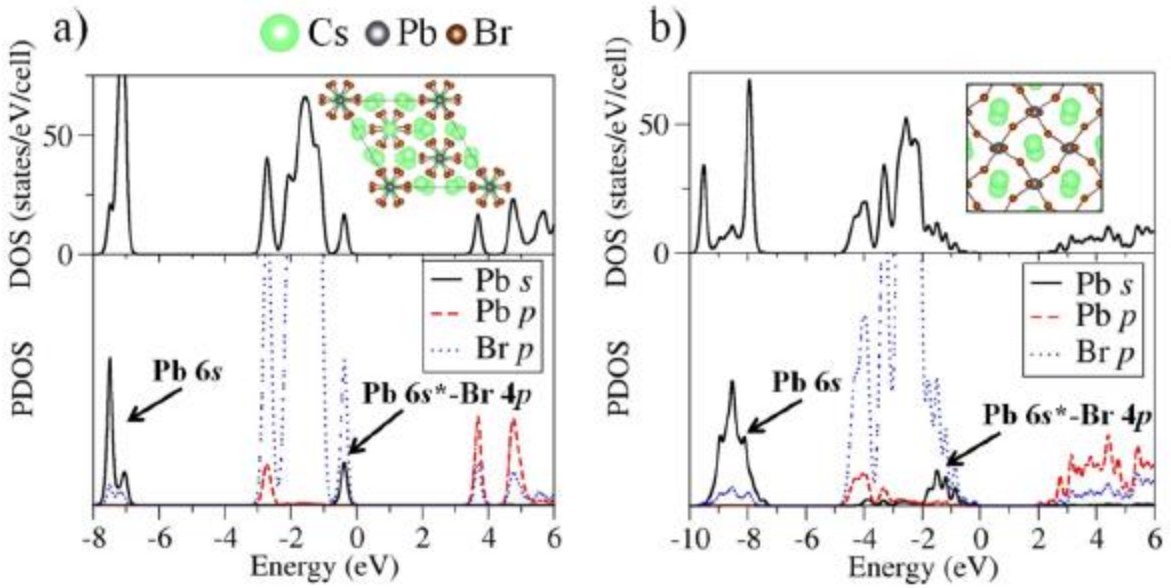
BE=-0.6eV :
not stable



- Setting NELEC to simulate a hole
- The hole couple with lattice distortion gaining BE

[1] **B. Kang**, and K. Biswas, J.Phys.Chem.Lett. 9 830 (2018) [2] **B. Kang**, and K. Biswas, J.Phys.Chem.C 120 12187 (2016)
[3] **B. Kang**, and K. Biswas, J.Phys.Chem.C 121 8319 (2017) **B. Kang**, and K. Biswas, Phys.Chem.Chem.Phys. 19 27184 (2017)

Possible calculations for Cs4PbBr6/CsPbBr3– VASP



DOS using Hybrid functionals and including spin-orbital coupling

Table 1. Calculated Static Dielectric Constants and Born Effective Charge of Cs_4PbBr_6 and $CsPbBr_3$[a]

Cs_4PbBr_6 static dielectric constants (ε_0^{xx} = 5.79, ε_0^{yy} = 5.79, ε_0^{zz} = 5.80)	
atom type	Born effective charge tensor (*xx*, *yy*, *zz*)
Cs_I (6a)	(1.23, 1.22, 1.21)
Cs_{II} (18e)	(1.37, 1.37, 1.19)
Pb (6b)	(2.91, 2.91, 2.91)
Br (36f)	(−1.08, −1.92, −1.04)
$CsPbBr_3$ static dielectric constants (ε_0^{xx} = 20.67,ε_0^{yy} = 22.84, ε_0^{zz} = 20.45)	
atom type	Born effective charge tensor (*xx*, *yy*, *zz*)
Cs (4c)	(1.28, 1.28, 1.31)
Pb (4b)	**(3.81, 4.02, 4.03)**
Br_{eq} (8d)	**(−2.17, −2.33,** −0.78)
Br_{ap} (4c)	(−0.81, −0.72, **−3.83**)

[a]Wyckoff positions are shown in parentheses beside the atoms to distinguish crystallographic sites. In the case of $CsPbBr_3$, Br_{eq} and Br_{ap} refer to Br ions at equatorial and apical location in the $[PbBr_6]$ octahedra.

[1] **B. Kang**, and K. Biswas, J.Phys.Chem.Lett. 9 830 (2018)

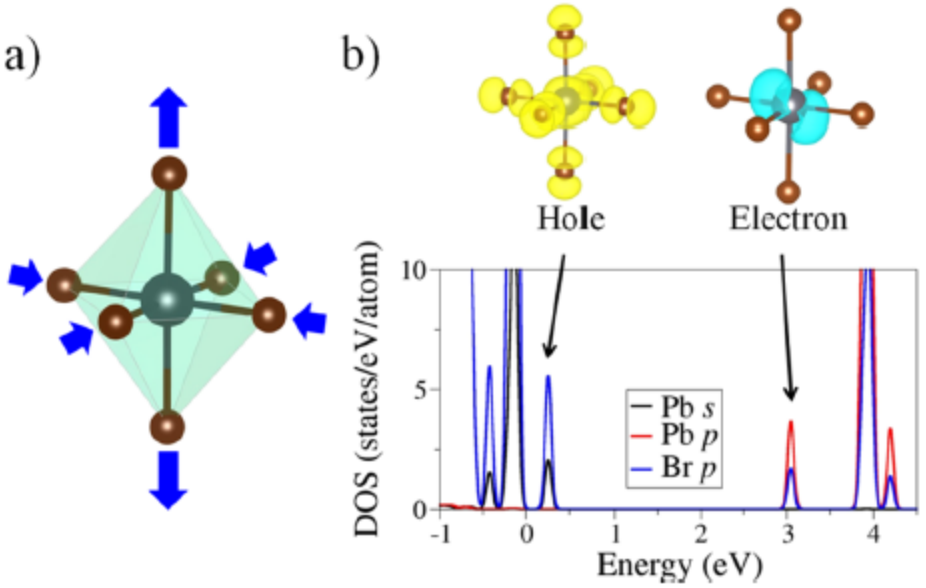


Figure 3. (a) Calculated structure of a self-trapped exciton (STE). Inward relaxation of four Br ions on equatorial plane and outward relaxation of two remaining Br ions in the axial direction are shown by arrows. (b) Calculated electronic DOS of STE structure shows unoccupied hole state (Br p + Pb s) and singly occupied electron state (Pb p + Br p) appearing inside the band gap.

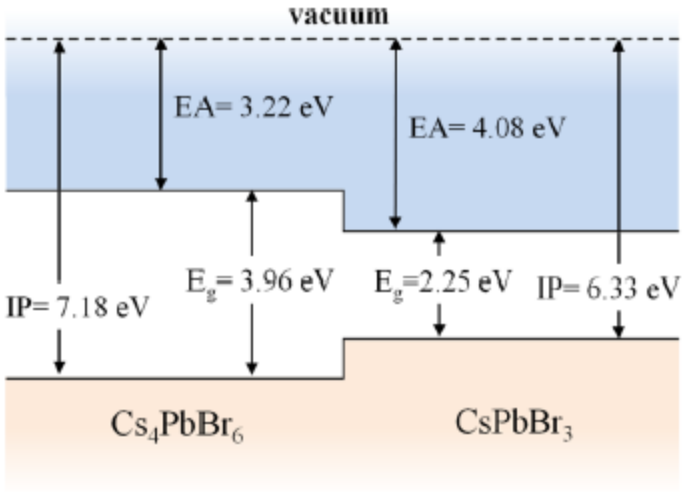


Figure 4. Calculated ionization potential (IP) and electron affinity (EA) relative to the vacuum level (dashed line). Experiment band gaps[3,5,6] are used to align CBMs of Cs_4PbBr_6 and $CsPbBr_3$.

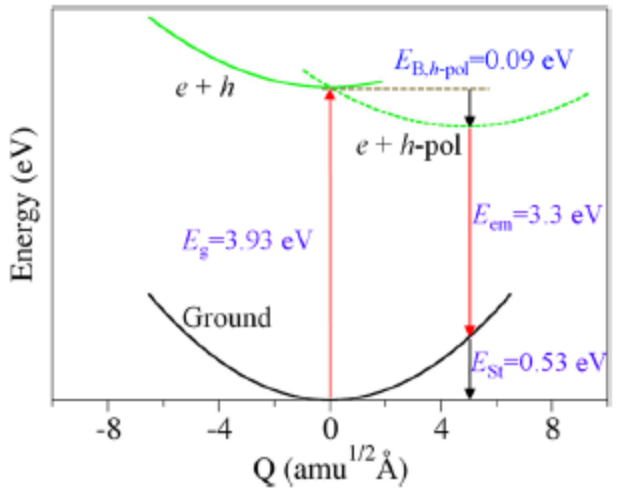


Figure 5. Configuration coordinate diagram showing emission around 3.3 eV due to conduction electron recombining with a hole polaron.

[1] **B. Kang**, and K. Biswas, J.Phys.Chem.Lett. 9 830 (2018)

Doping on Carbon Nano Dots – VASP, G09

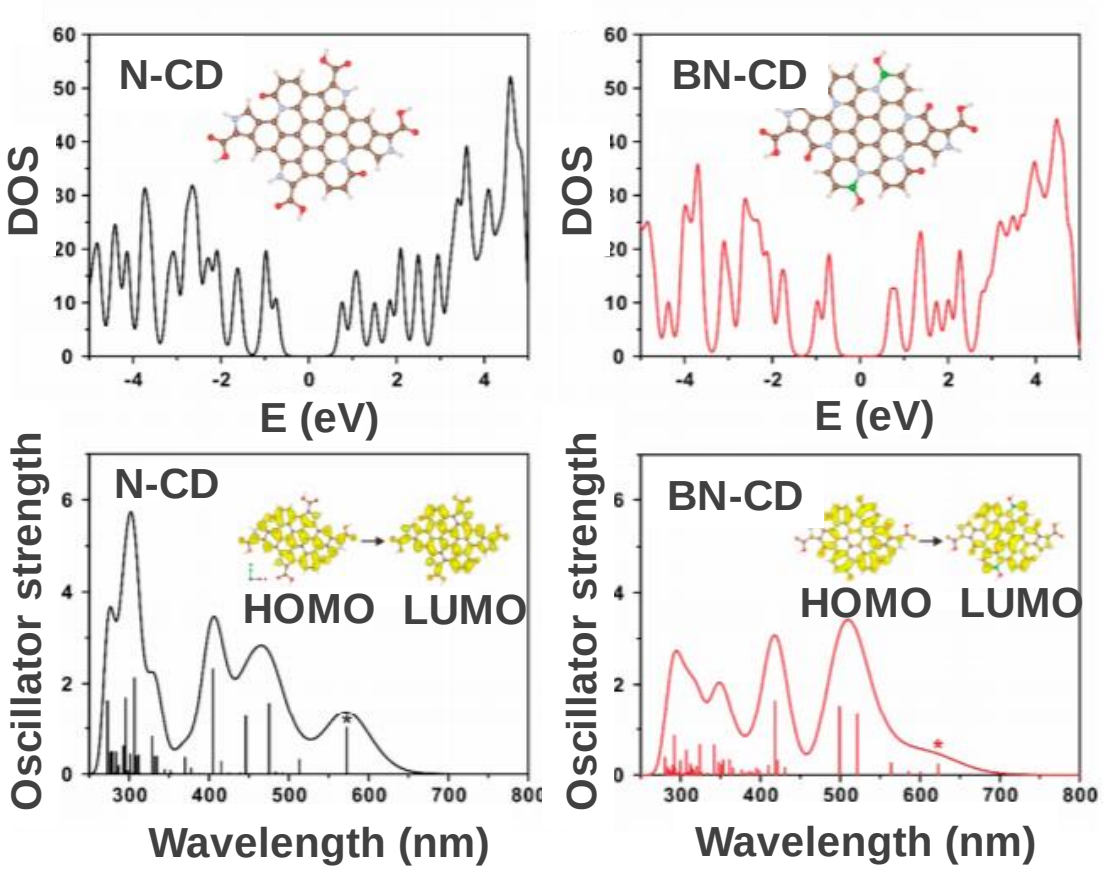
Finding structure (VASP), oscillator strength (TD-DFT,G09)

Nitrogen doped Carbon Nanodots

Boron and Nitrogen doped Carbon Nanodots

Elemental composition of CDs determined by XPS (X-ray photoelectron spectroscopy)

	N-CD	BN-CD
C	64.47	48.85
O	21.89	35.49
N	13.64	12.16
B	-	3.51
C/O	2.94	1.37
C/N	4.72	4.02

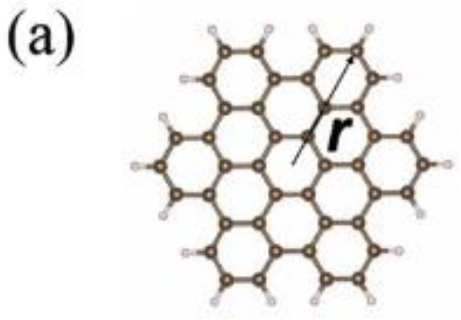


- B&N-CDs exhibit PL twice larger than N-CDs
- With clue of elemental analysis by XPS, DFT can find stable structure with many trials of configurations.
- Calculated Oscillator strength using TD-DFT (G09)

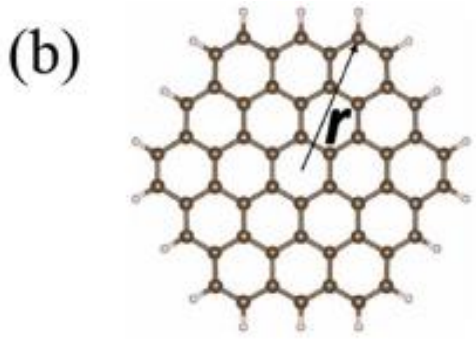
[1] Y. Choi, **B. Kang**, G.S Lee and B.S. Kim et al. Chem. Matter. 28, 6840 (2016)

Enhanced PL in edge-functionalized sp2 carbon cluster–VASP, G09

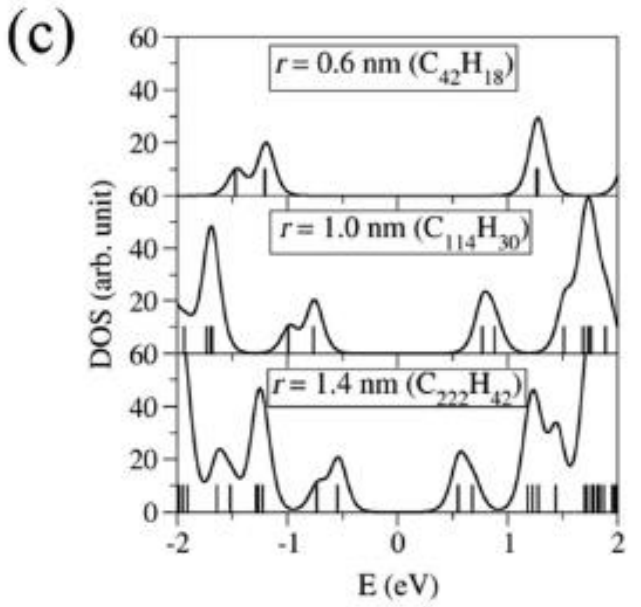
Construct Graphene quantum dots (GQD)

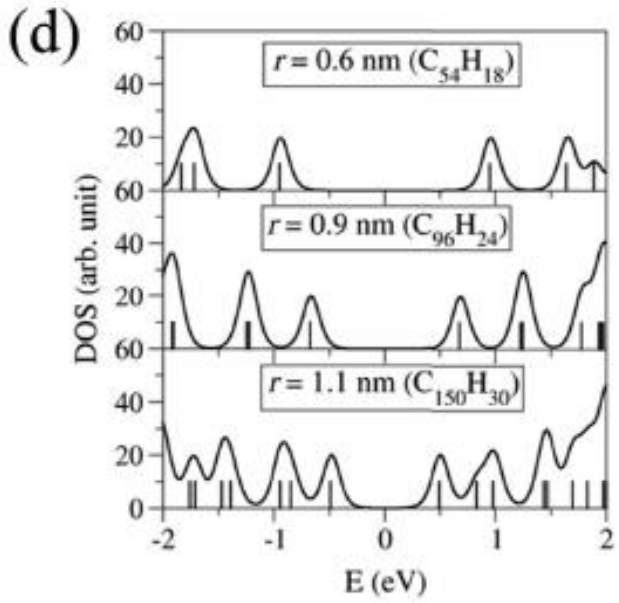


armchair



zigzag

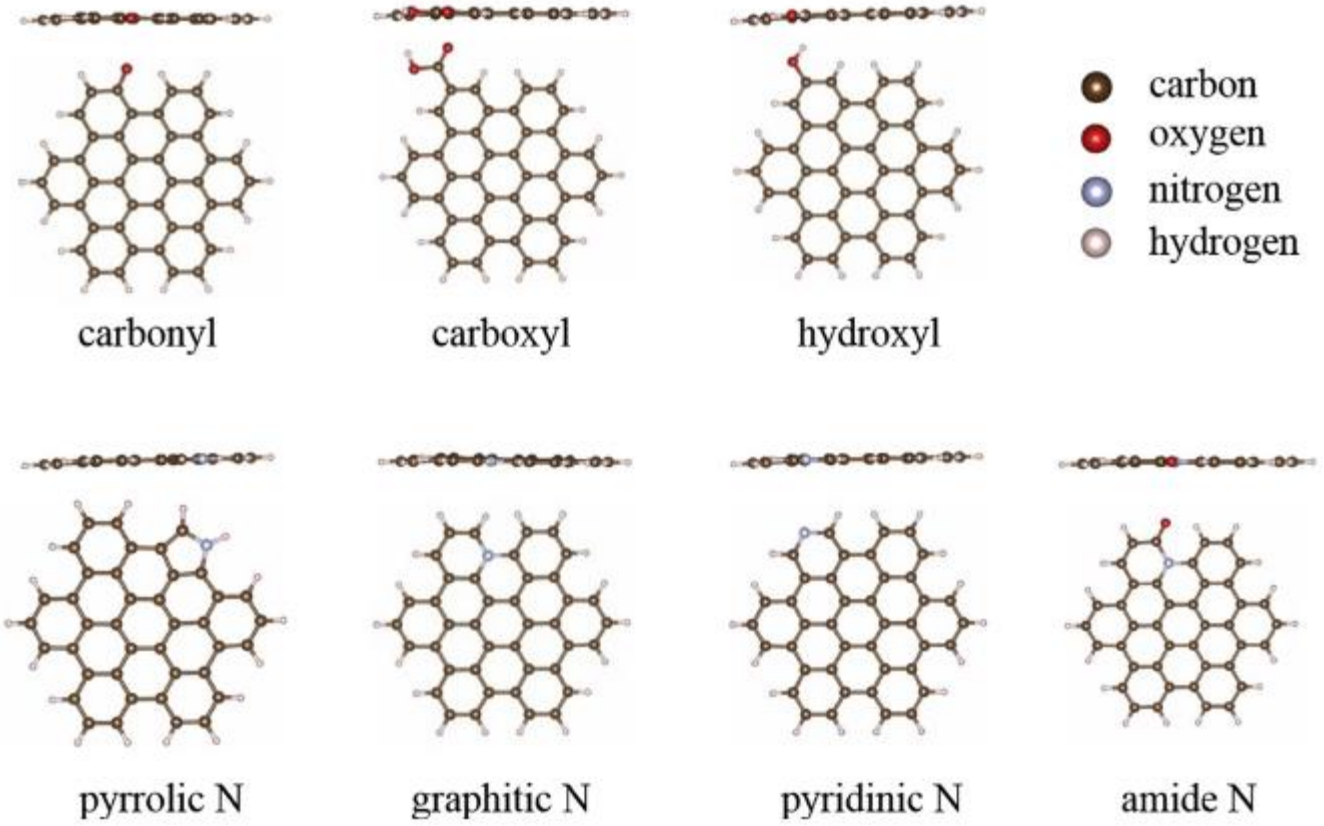




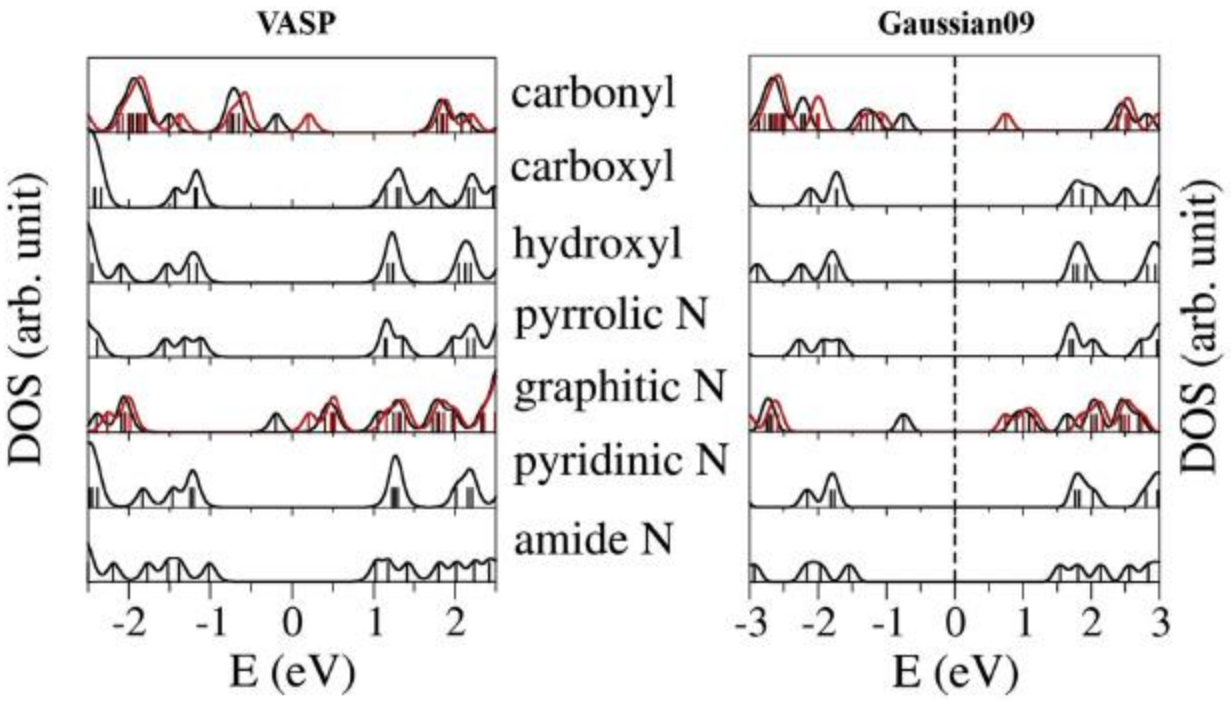
- Two type of edge
- Increasing size reduce gap

[1] **B. Kang**, et al., Carbon 109 418 (2016)

Edge functionalization (most stable configuration)



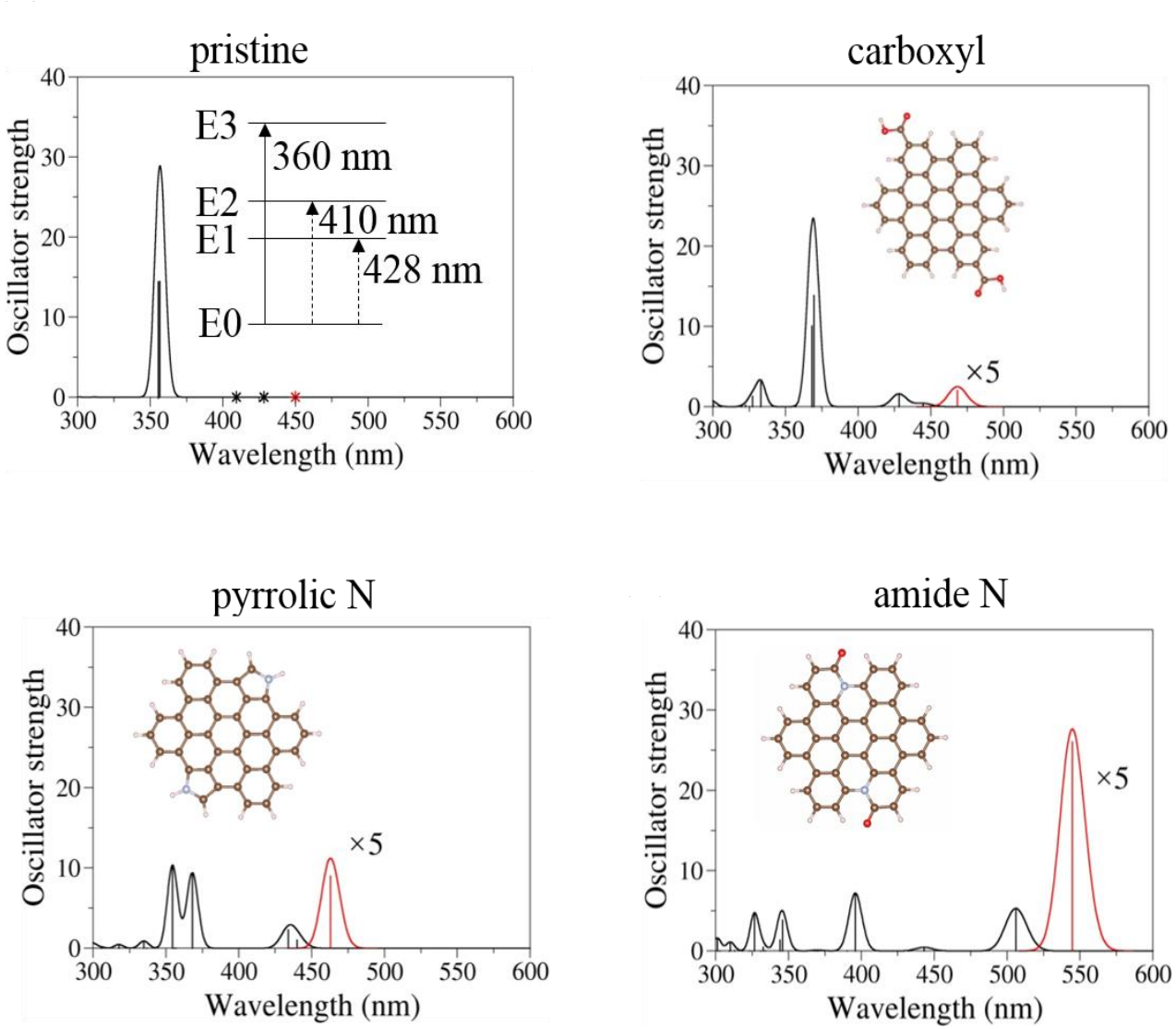
black: up, red: down spin



- Geometry optimization for various configurations is needed.
- LSDA (VASP) underestimated the band gap in comparison to B3LYP (G09)
- Character of HOMO and LUMO are consistent in Both.

[1] **B. Kang**, et al., Carbon 109 418 (2016)

Oscillator strengths (B3LYP/TD-DFT)



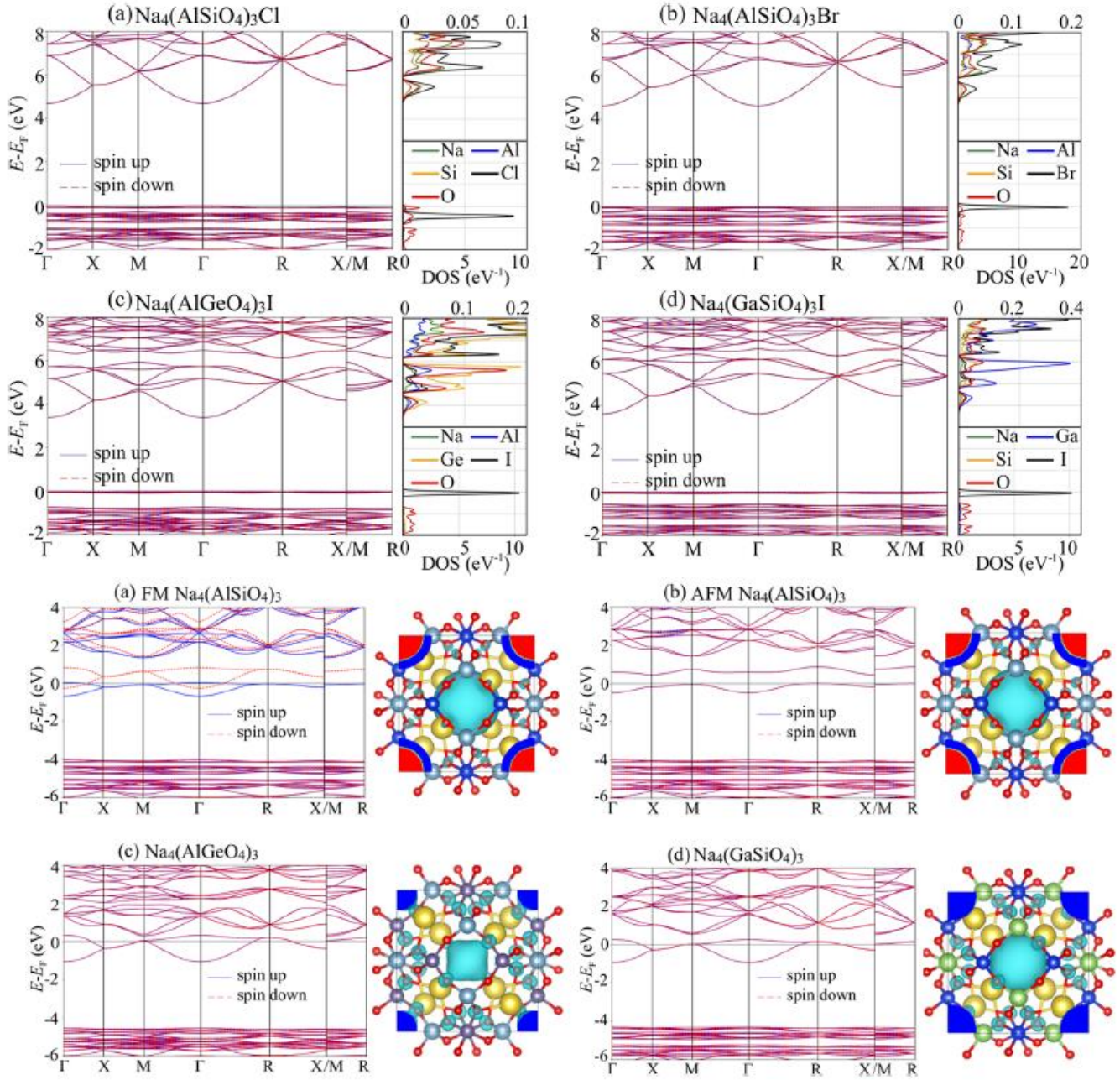
- In pristine, transition is forbidden due to selection rule of symmetric HOMO and LUMO
- Alter HOMO & LUMO by edge functionalization -> rise transition amplitude

Calculated oscillator strengths for the absorption (black) and the emission (red) by B3LYP/TD-DFT.

[1] **B. Kang**, et al., Carbon 109 418 (2016)

Electrides derived from sodalites – VASP

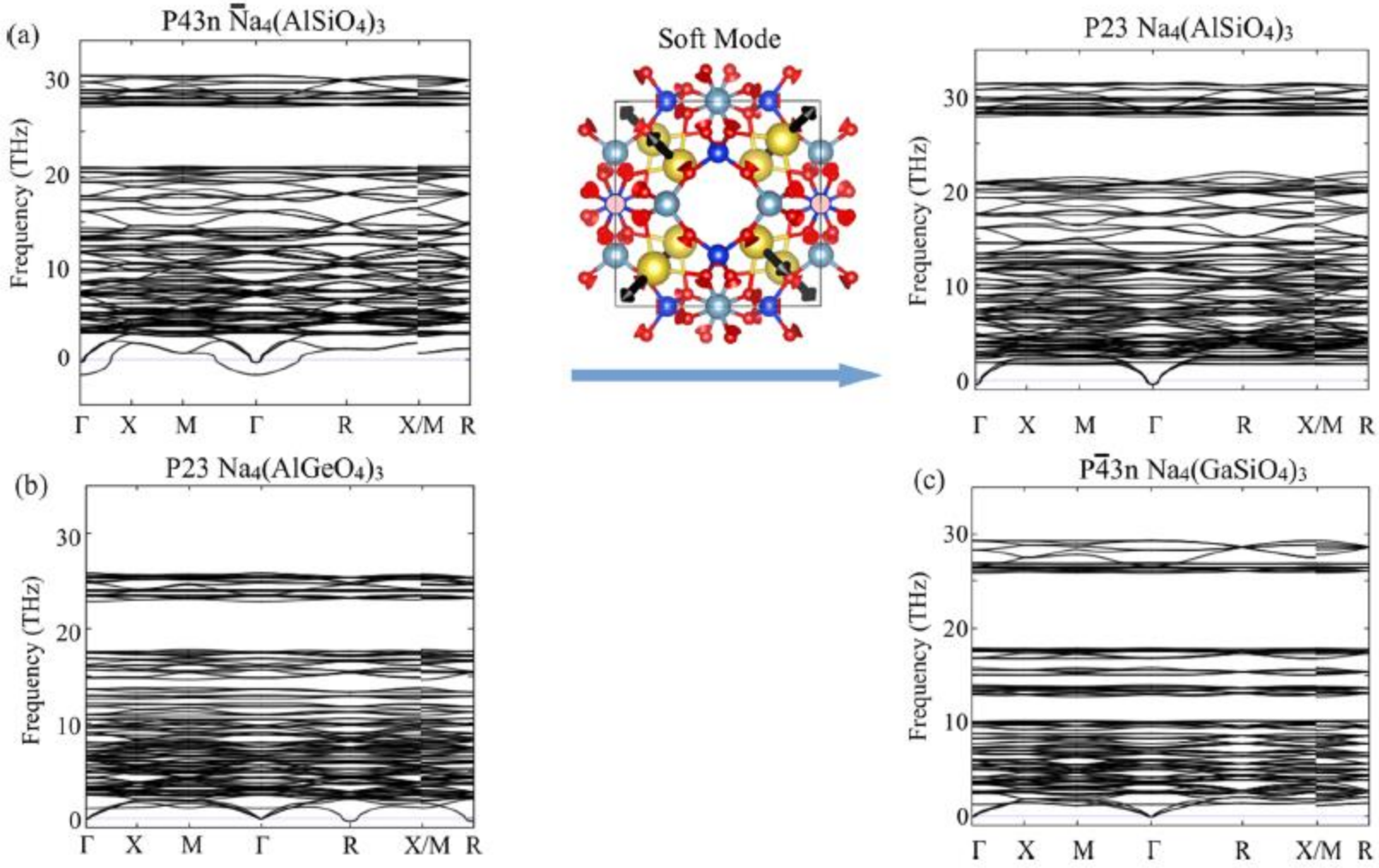
Finding structure removing halide



- Created electrides removing halide
- The excess electrons are localized at the crystal cages and form electride bands
- For $Na_4(AlSiO_4)_3$, AFM configuration has a lower energy of 33 meV per formula unit than the FM configuration.

[1] **B. Kang** et al J. Phys. Chem. C. 127, 18745 (2023)

Phonon – finding stable structure

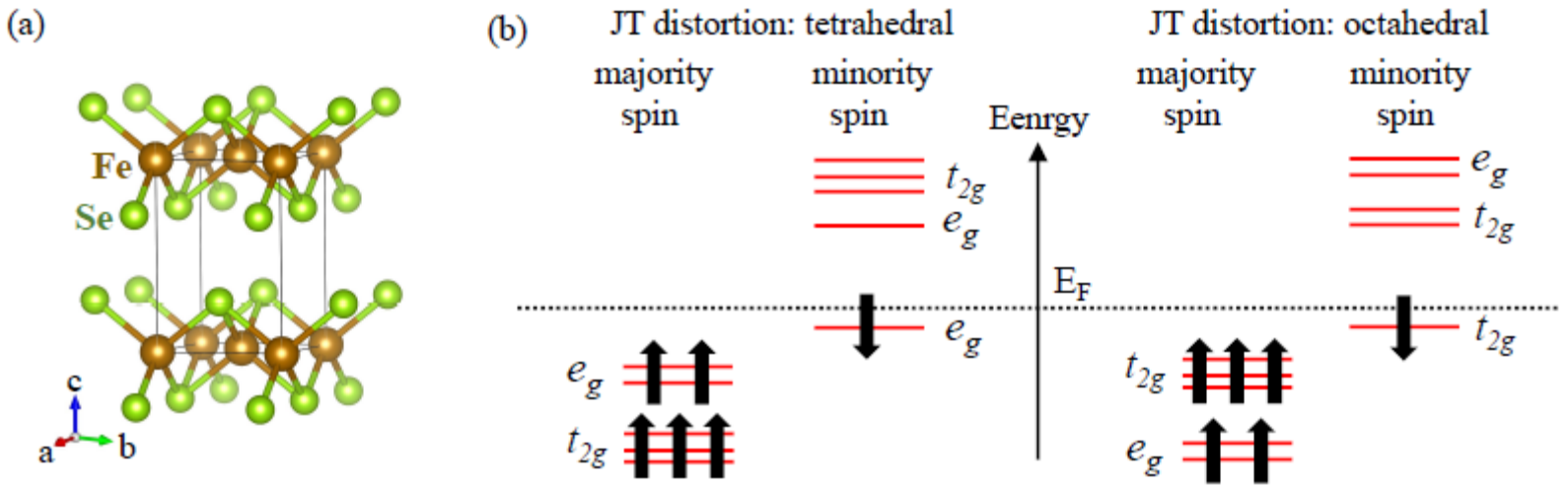


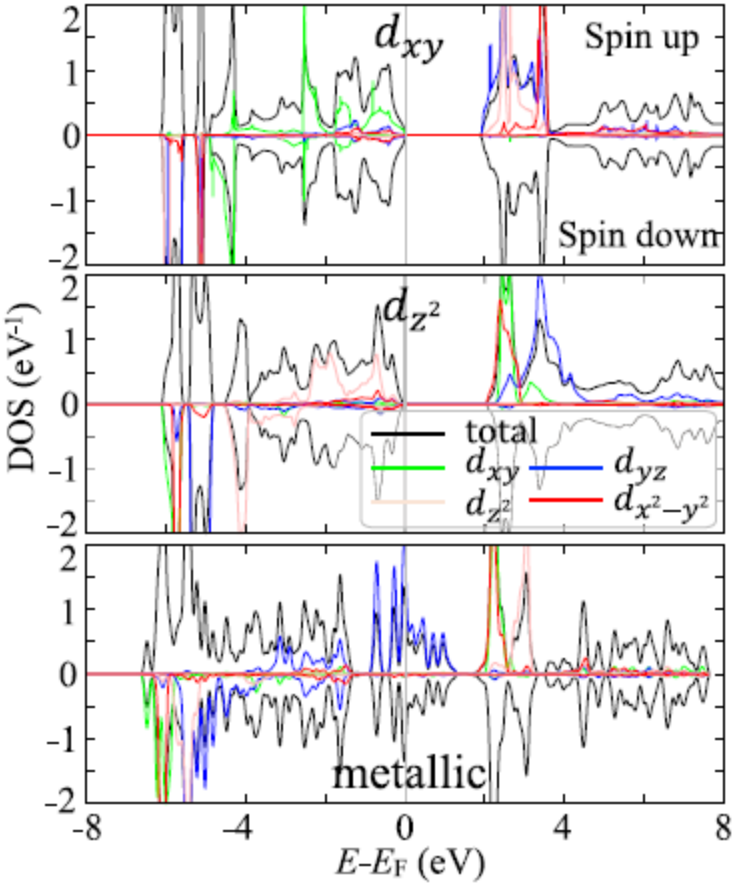
- Used Phonopy and VASP
- Using soft mode can remove negative phonon.

[1] **B. Kang** et al J. Phys. Chem. C. 127, 18745 (2023)

Mott-insulator state of Van der Waals 2D FeSe – VASP, LQSGW+DMFT, GW+EDMFT

Insulating electronic structure (VASP)





- Lower levels of minority spin are degenerate.
- Jahn-Teller distortion remove the degeneracy
- DFT+U (=5 eV), AFM
- Insulating states show lower total energy than metallic state
- Electronic structure is not uniquely defined.

[1] **B. Kang** et al Phys. Rev. Lett. 132, 266506 (2024)

Thank you