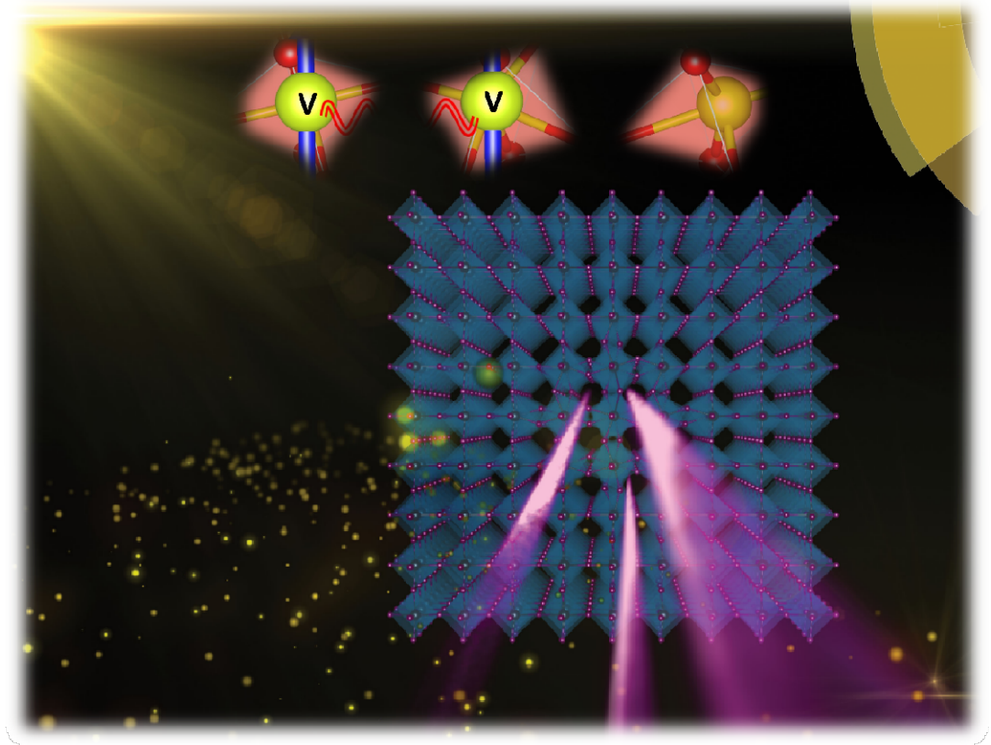
Testing: DFT applications in Physics and Chemistry and their technical aspects



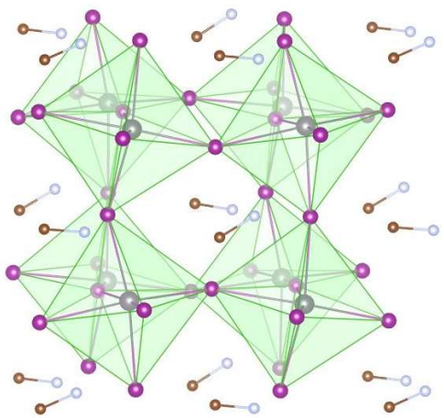
Byungkyun Kang

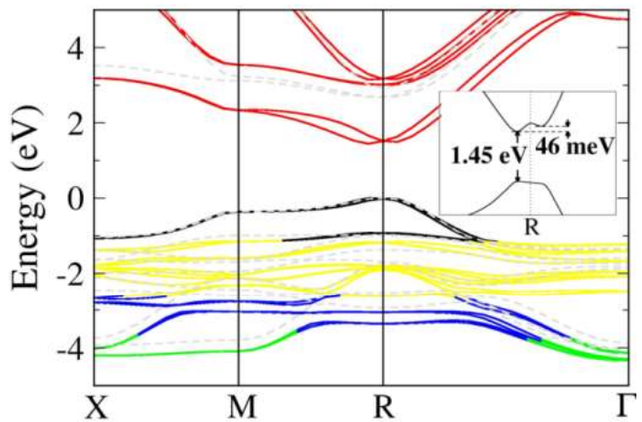
bkang@udeledu

Contents

First-Principles Methods for real materials

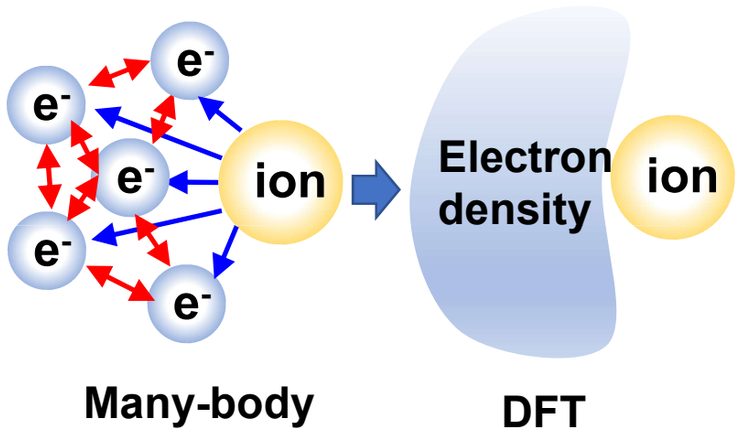
- Density functional theory
- No empirical parameter
- Incorporating rapidly growing computer power





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

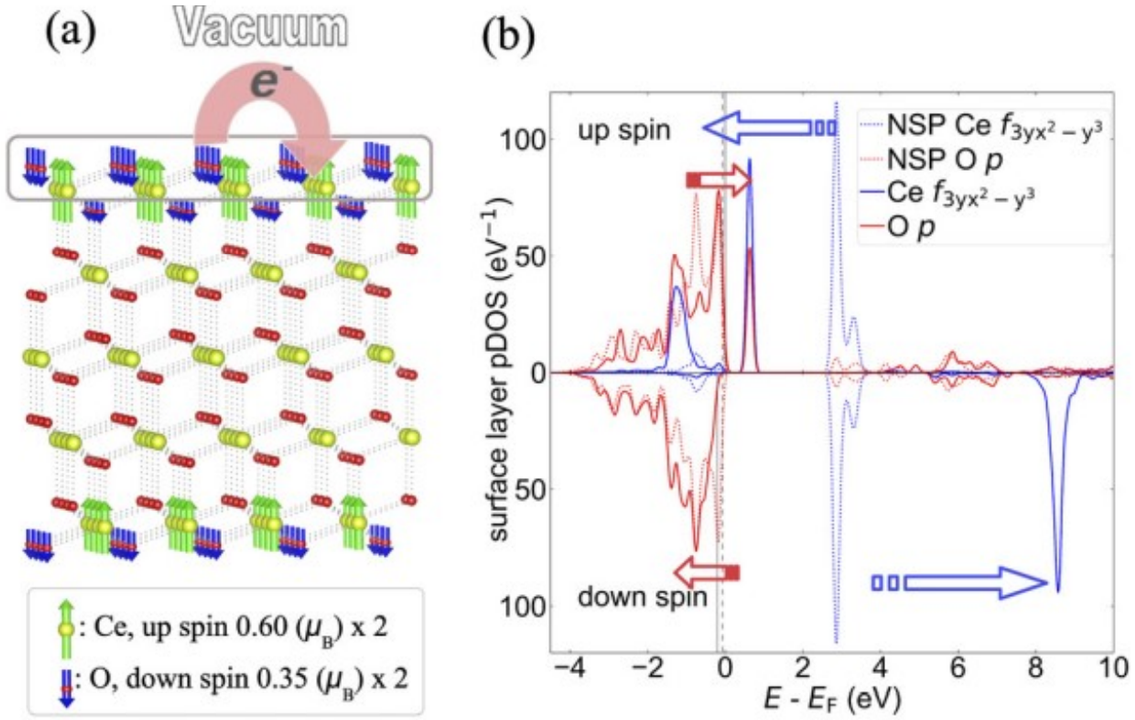
- VASP
- CASTEP
- CPMD
- ABINIT – GPL
- BigDFT – GPL – wavelets
- Quantum-Espresso (formerly PWscf) – GPL
- PEtot – GPL
- DACAPO – GPL
- Socorro – GPL
- JDFTx formerly known as DFT++ – GPL
- Paratec
- PARSEC – GPL – real space, pseudopotential
- CP2K – GPL (mixed basis DFT)
- GPAW – GPL – real-space 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

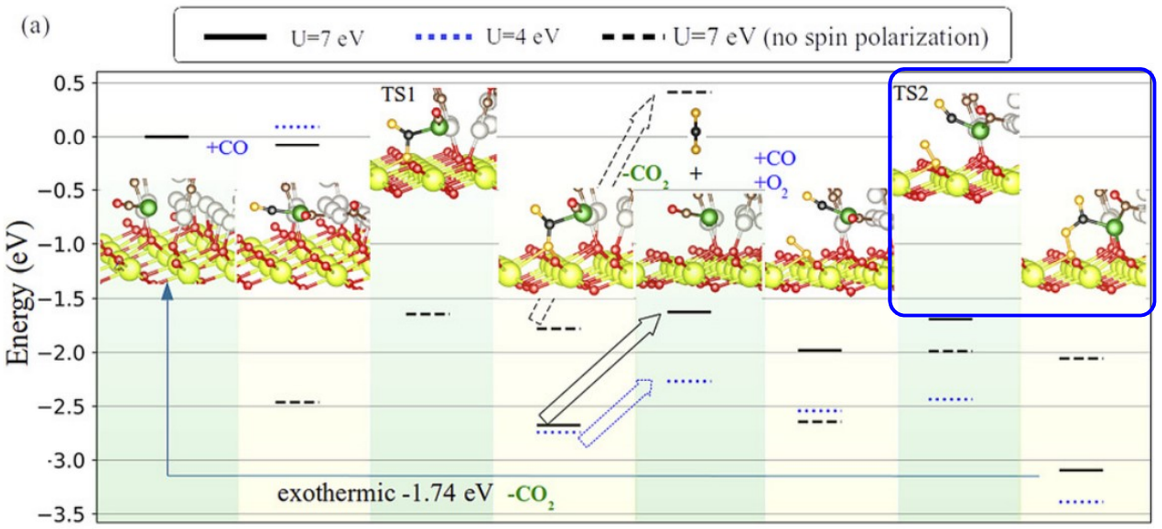


- Construct O terminated supercell with enough vacuum
- Set U in DFT+U
- Set initial spin configuration

```
&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)

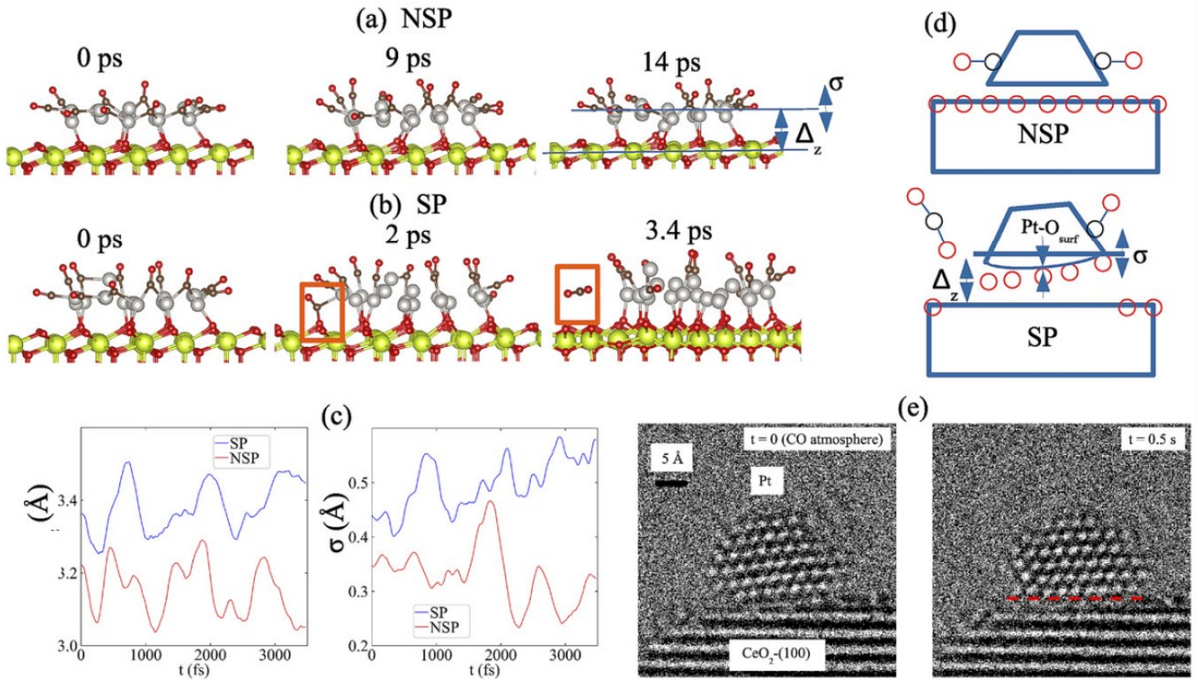


- Prepare optimized init and final xyz
- Set number of images
- Find activation barrier

```
&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

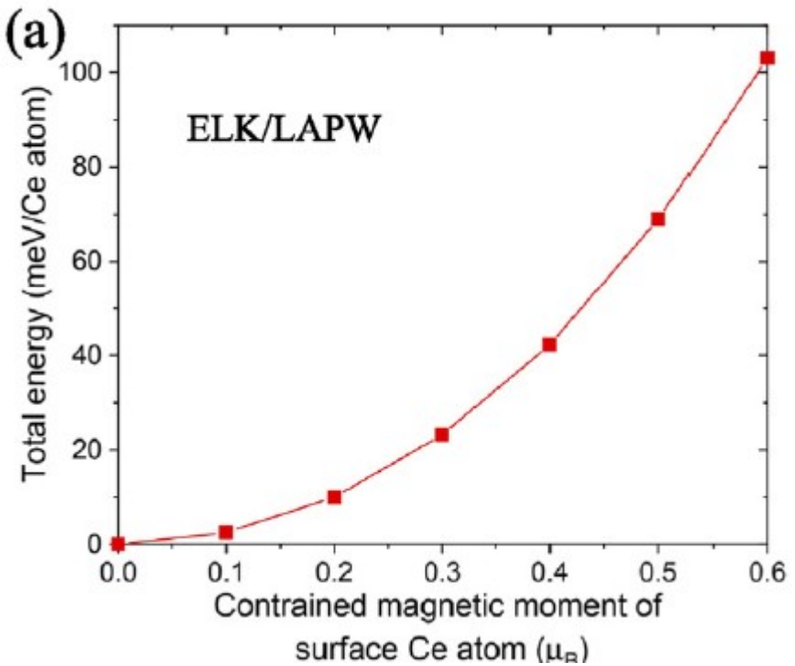


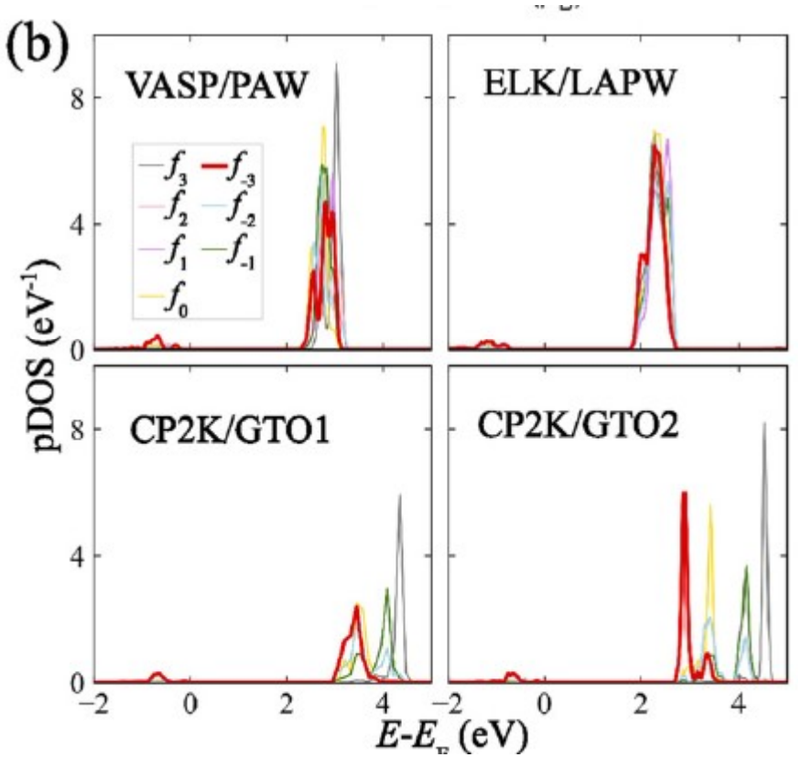
- Set temperature, time step, etc.
- ~1000 atoms geometry optimization on HPC
- ~500 atoms ab-initio MD on HPC
- Surface ferromagnetism explain experiments

```
&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

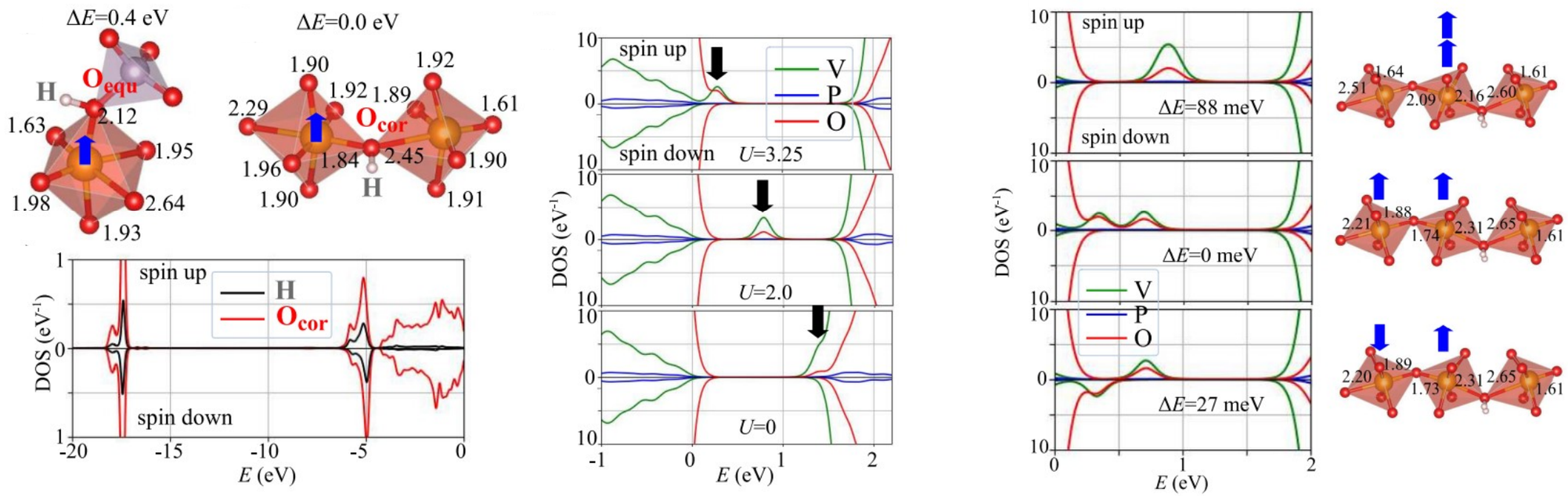


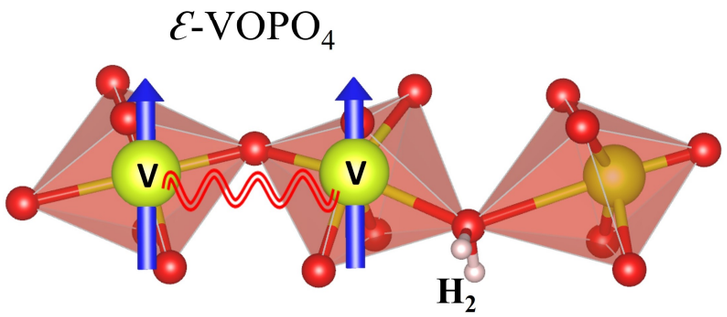


- Set temperature, time step, etc.
- ~1000 atoms geometry optimization on HPC
- ~500 atoms ab-initio MD on HPC
- Surface ferromagnetism explain experiments

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

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

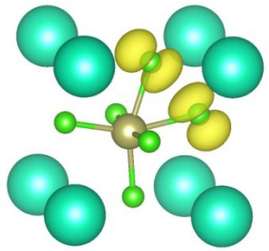




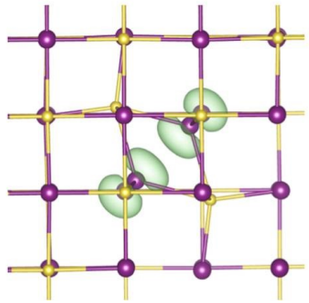
- ~300 atoms simulations on HPC
- Short-range spin-spin interaction
- Homogeneous magnetization

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

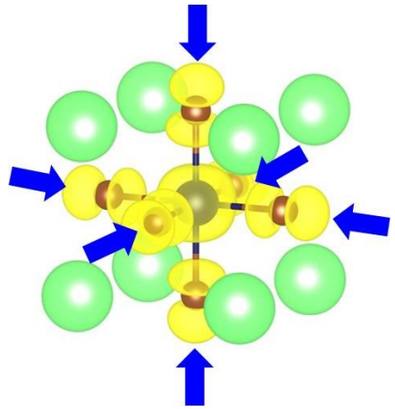
Small polarons using Hybrid functional – VASP



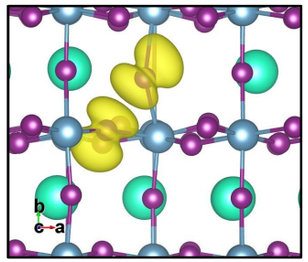
Cs_2HfCl_6
Binding E=0.71 eV



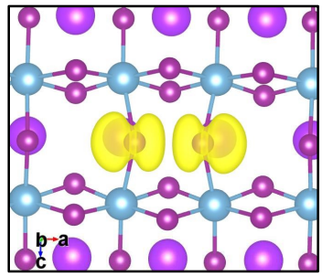
NaI
BE=0.19 eV



Cs_4PbBr_6
BE=0.09 eV

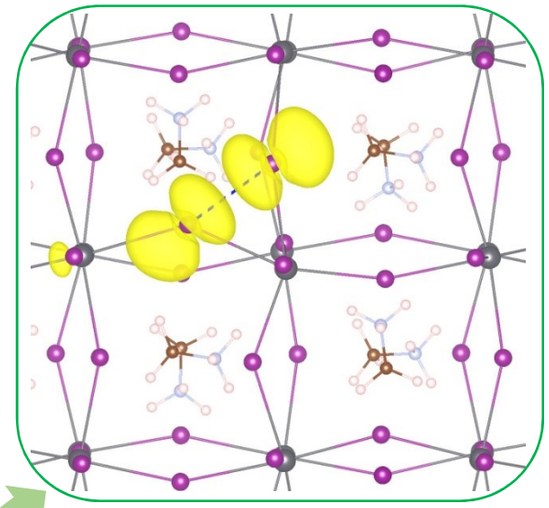


$CsCaI_3$
BE=0.16 eV

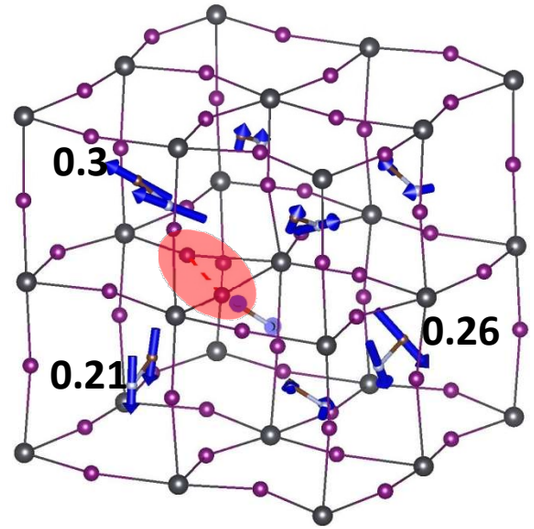


$KCaI_3$
BE=0.07 eV

$CH_3NH_3PbI_3$



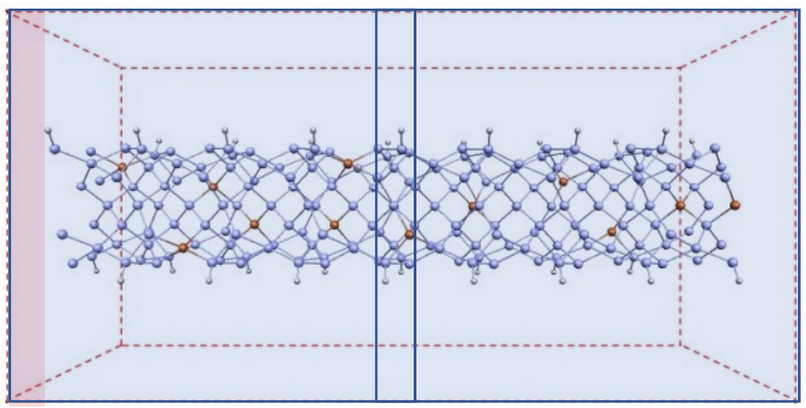
BE=-0.6eV :
not stable



- Hybrid functional, ~200 atoms, HPC ≈ small cluster

[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)

Thermal Conductivity of silicon nanowire -SIESTA



Using DFT

construct nanowire

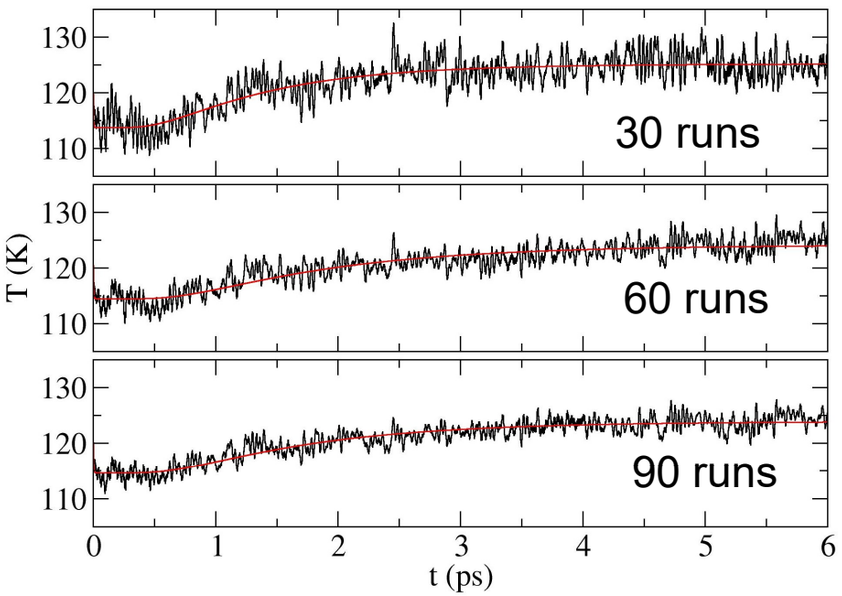
Calculate normal modes

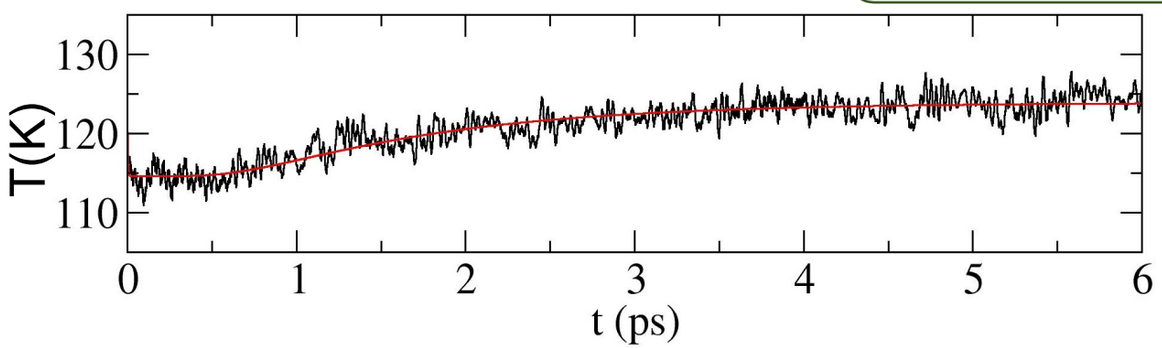
Prepare hot & cold slices

Run ab-initio MD

Monitor temperature

initial phases: randomly generated (must average)
no thermalization, no thermostat

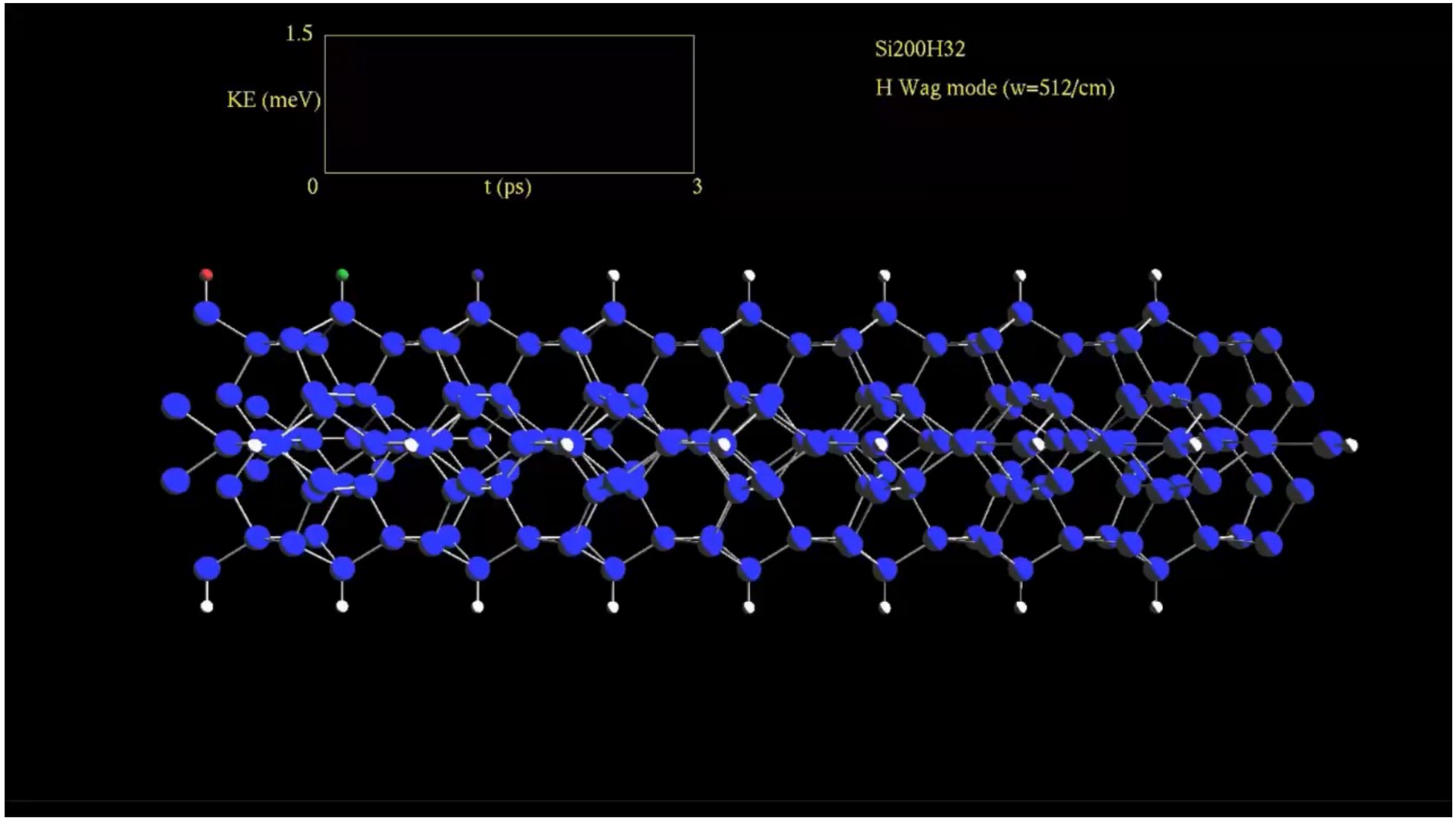




- Each job used 12 processes in HPC
- Run ~100 jobs simultaneously
- Need to script automatic restart

[1] **B. Kang**, and S.K. Estreicher, Phys. Rev. B 89, 155409 (2014)

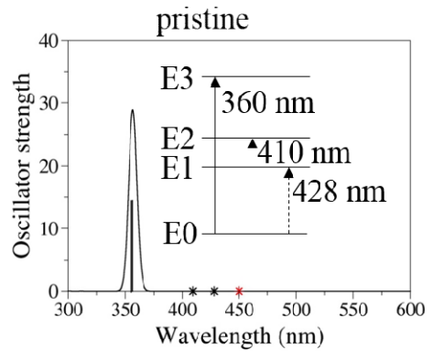
Visualize surface phonon

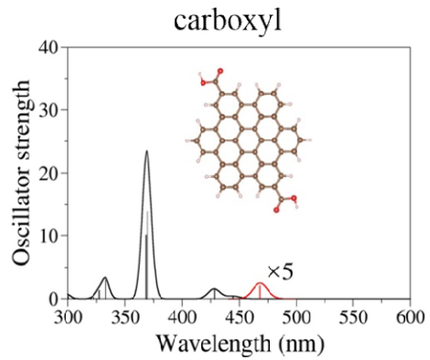


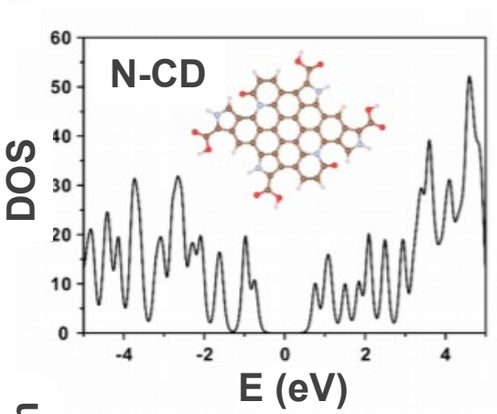
Doping on Carbon Nano Dots – G09

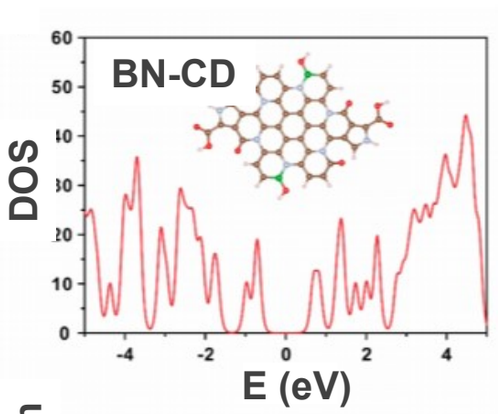
Nitrogen doped Carbon Nanodots

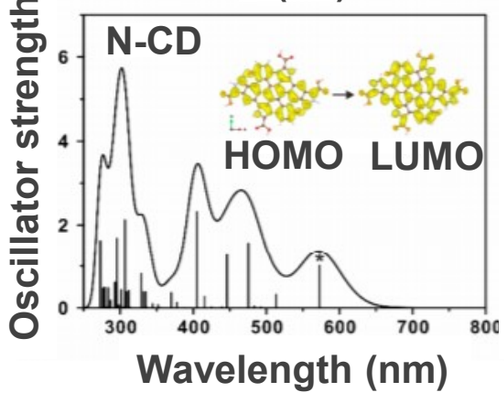
Boron and Nitrogen doped Carbon Nanodots

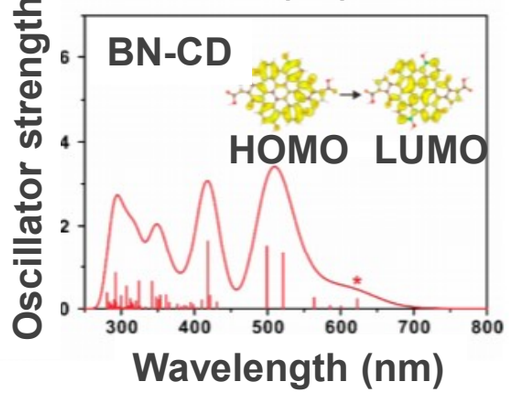


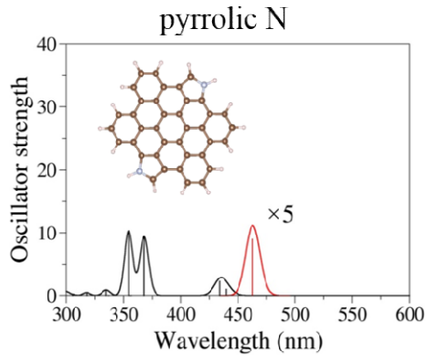


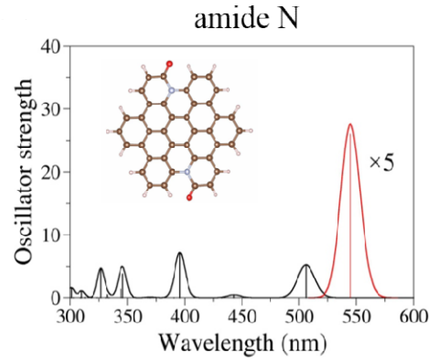












- Found structures
- Calculated Oscillator strength
- Alter HOMO & LUMO -> rise transition amplitude
- Used small cluster
- Maximum performance in one node

[1] **B. Kang**, et al., Carbon 109 418 (2016)
[2] Y. Choi, **B. Kang**, G.S Lee and B.S. Kim et al. Chem. Matter. 28, 6840 (2016)