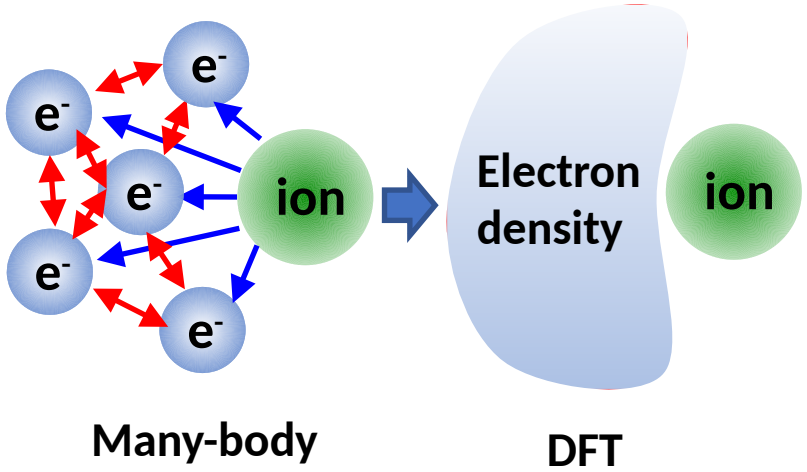
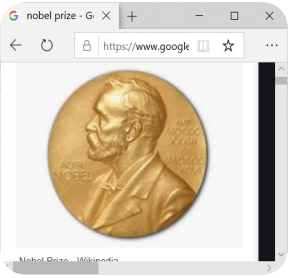
Density functional theory and VASP

Byungkyun Kang

Density Functional Theory



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



Hohenberg and Kohn

• First Hohenberg-Kohn theorem:
The ground state properties of a many-electron system depend only on the electronic density n(x,y,z)

• Second Hohenberg-Kohn theorem:
The correct ground state density for a system is the one that minimizes the total energy through the functional E[n(x,y,z)]

• A functional is just a function that depends on a function

Form of the Density Functional

$$\hat{H}_{el} = \hat{T}_e + \hat{V}_{eN} + \hat{V}_{ee}$$

$$E[\rho] = T[\rho] + E_{eN}[\rho] + E_{ee}[\rho]$$

$$E_{eN}[\rho] = \sum_A \int \frac{Z_A \rho(\vec{r})}{|\vec{R}_A - \vec{r}|} d\vec{r}$$

$$J[\rho] = \frac{1}{2} \int \int \frac{\rho(\vec{r})\rho(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r} d\vec{r}'$$

Kohn-Sham Kinetic Energy

$$\begin{aligned} T_s[\rho] &= \sum_{i=1}^{N} \langle \phi_i | -\frac{1}{2}\nabla^2 | \phi_i \rangle, \\ \rho(\vec{r}) &= \sum_{i=1}^{N} |\phi_i(\vec{r})|^2. \end{aligned}$$

$$\begin{aligned} E_{\mathrm{KS-DFT}}[\rho] &= T_s[\rho] + E_{eN}[\rho] + J[\rho] + E_{xc}[\rho], \\ E_{xc}[\rho] &= (T[\rho] - T_s[\rho]) + (E_{ee}[\rho] - J[\rho]). \end{aligned}$$

Form of the Density Functional

- So what's the density functional actually look like?

- The Coulomb interaction for a given density interacting the nuclei is very straightforward to compute; so is the Coulomb interaction of the density with itself (J term)

- Coulomb (J) terms are great, but we also need to account for electron antisymmetry (exchange effects) and electron correlation effects

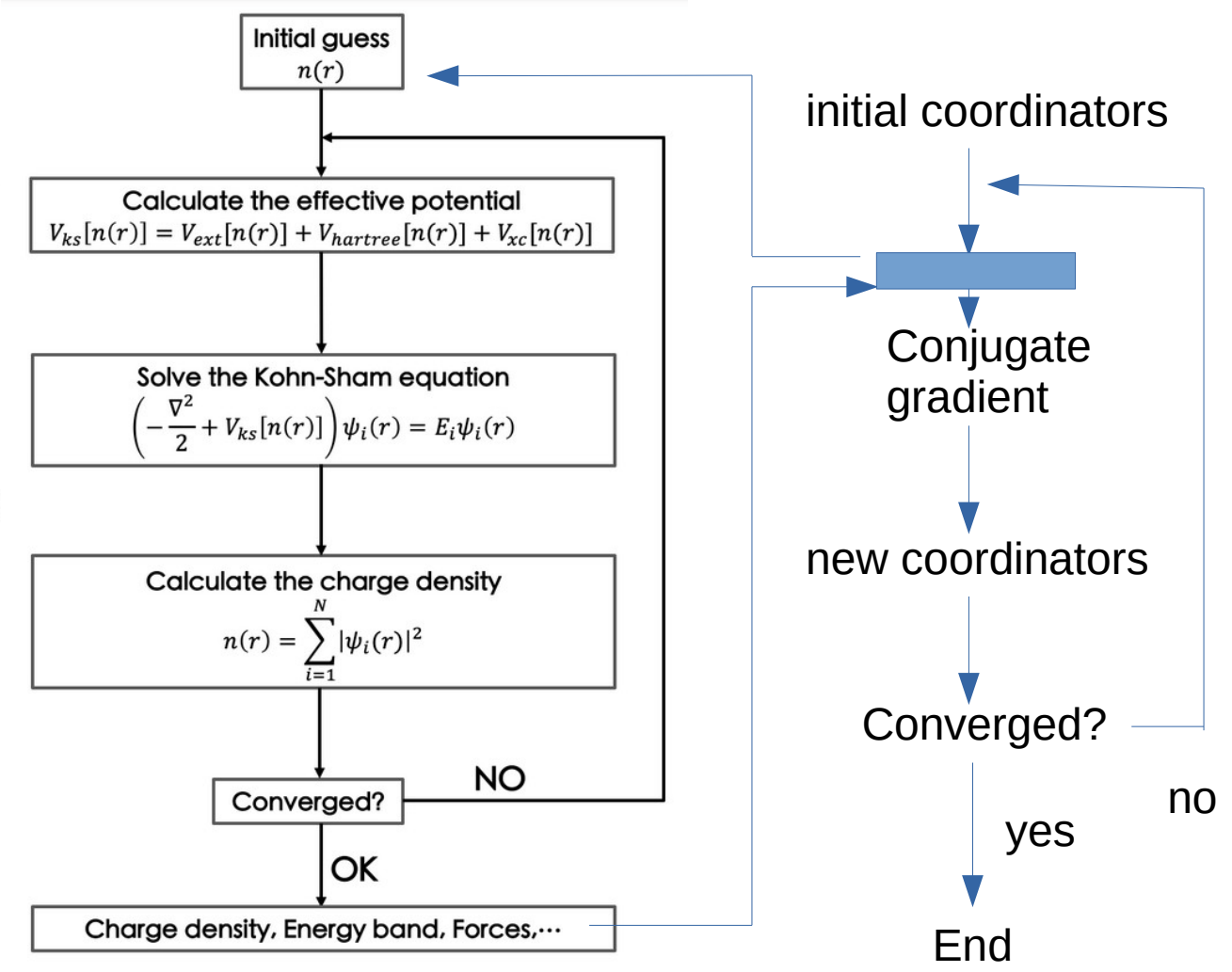
- Additionally, not clear how to compute kinetic energy as a function of the density

- We can compute every piece of a Kohn-Sham DFT
energy exactly except for the "exchange-correlation" piece, E xc [ρ].
- Unfortunately the exact exchange-correlation energy functional is not known and is probably so
complicated that even if it were known it would not be computationally useful
- Hence, use various approximate exchange-correlation functionals (S-VWN, B3LYP, etc.)

Kohn-Sham DFT Self-Consistent-Field Equations

$$\hat{h}_{KS}(\vec{r})\phi_i(\vec{r}) = \epsilon_i\phi_i(\vec{r}),$$
$$\hat{h}_{KS}(\vec{r}) = -\frac{1}{2}\nabla^2(\vec{r}) + V_{eff}(\vec{r}),$$
$$V_{eff}(\vec{r}) = V_{eN}(\vec{r}) + \int \frac{\rho(\vec{r}')}{|\vec{r}-\vec{r}'|}d\vec{r}' + V_{xc}(\vec{r})$$

- Much like Hartree-Fock but there's an extra "exchange-correlation" piece that adds approximate electron correlation and can handle the exchange term differently



Atomic DFT code

the electron states :spherical harmonic functions and radial functions

$$\psi_{nlm}(r) = Y_{lm}(\theta,\phi) r^{-1} u_{nl}(r)$$

Schrodinger equation

$$\left(-\frac{1}{2}\frac{d^2}{dr^2} u_{nl}(r) + \frac{l(l+1)}{2r^2} + V_{KS}(r) \right) u_{nl}(r) = \varepsilon_{nl} u_{nl}(r)$$

$$V_{KS} = V_{ext}(r) + V_H + V_{xc}$$

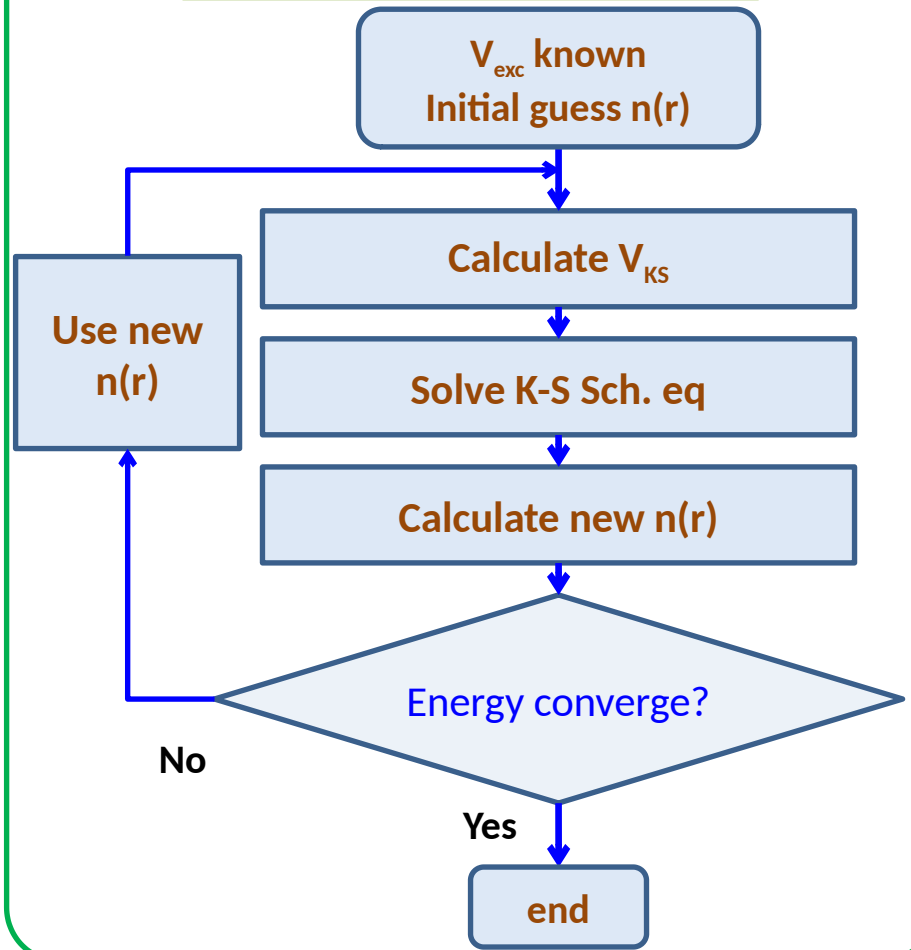
Self consistently solved using Numerov's method

V_{xc} : Ceperley-Alder exchange-correlation functional

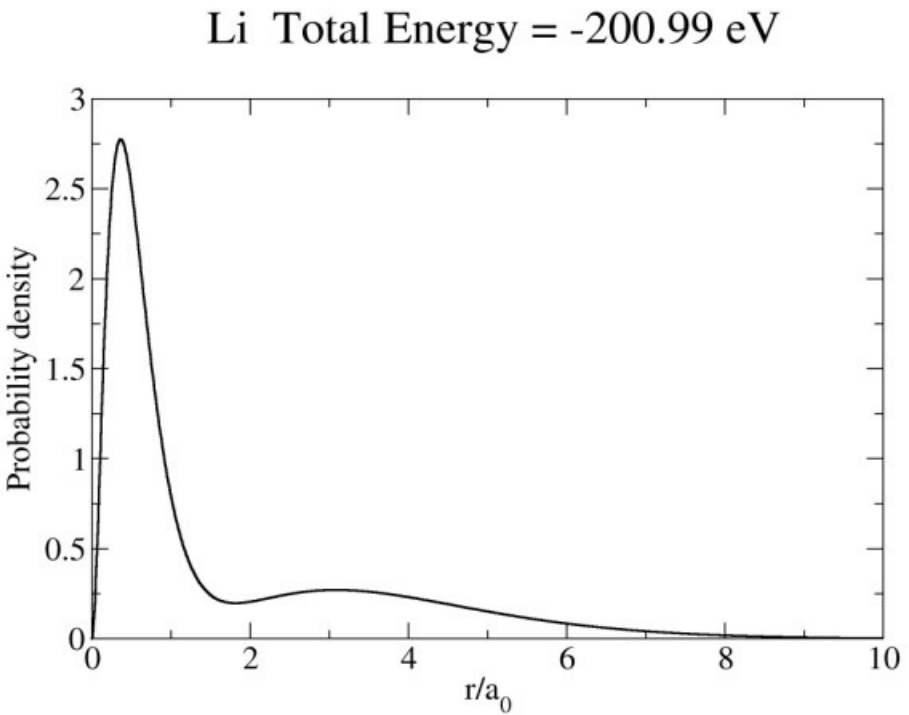
In Perdew-Zunger parametrization

Atomic DFT code

Self consistent loop



result



general DFT

the electron states :spherical harmonic functions and radial functions

$$\psi_{nlm}(r) = Y_{lm}(\theta,\phi) r^{-1} u_{nl}(r)$$ → expand to plane wave or gausian basis.

need to set cut off

Schrodinger equation

$$\left(-\frac{1}{2}\frac{d^2}{dr^2} u_{nl}(r) + \frac{l(l+1)}{2r^2} + V_{KS}(r) \right) u_{nl}(r) = \varepsilon_{nl} u_{nl}(r)$$ → expand to lattice.

need to set K-grid

$$V_{KS} = V_{ext}(r) + V_H + V_{xc}$$ → need to choose exchange-correlation functional LDA or PBE ...

VASP- compile on stampede2

Copy one of the makefile.include.arch files in root/arch to root/makefile.include.
Take one that most closely reflects your system (hopefully). For instance, on a linux box with the Intel Composer suite

```
cp arch/makefile.include.linux_intel  ./makefile.include
```

```
make all
```

in bin

vasp_gam is the version of vasp working at the Gamma point only

vasp_std is standard version of vasp

vasp_ncl is for non-collinear calculations for instance to perform fully non-collinear magnetic structure calculations

or to include spin-orbit interactions in the calculations

VASP- run on stampede2

```
#!/bin/bash -l
#SBATCH -J cshfcl
#SBATCH -p skx-dev
#SBATCH -N 1
#SBATCH -t 2:00:00
#SBATCH --ntasks-per-node=48
#SBATCH --cpus-per-task=2

#module load vasp

ibrun --cpu-bind=cores vasp_std
```

four input files

INCAR

```
ENCUT = 300
ISMEAR = 0
SIGMA = 0.05
EDIFF = 1E-4
PREC = A
LREAL = A
```

smearing in eV

break condition

recommended

```
IBRION = 2
ISIF = 2
EDIFFG = -0.05
NSW = 100
```

2: ionci relaxation (conjugate gradient algorithm)
2: ionci relaxation (conjugate gradient algorithm)
break condition for the ionic relaxation loop

```
#ISPIN = 2
#NUPDOWN = 2
#NELECT = 1024
#ISYM = 0
```

```
#LHFCALC = .TRUE.
##HFSCREEN = 0.2
#ALGO = A
#TIME = 0.4
#PRECFOCK = F
```

```
#LVTOT = .TRUE.
#LAECHG = .TRUE.
LORBIT = 10
NEDOS = 5000
```

whether the PROCAR or PROOUT files are written.

POSCAR

```
POSCAR created by SUPERPOSCAR
   10.4200000000000
     1.0000000000000000    0.0000000000000000    0.0000000000000
     0.0000000000000000    1.0000000000000000    0.0000000000000
     0.0000000000000000    0.0000000000000000    1.0000000000000
   Cs   Hf   Cl
     8     4    24
Direct
  0.3500000000000000  0.2500000000000000  0.2500000000000000
  0.7500000000000000  0.7500000000000000  0.7500000000000000
  0.2500000000000000  0.7500000000000000  0.7500000000000000
  0.7500000000000000  0.2500000000000000  0.2500000000000000
  0.7500000000000000  0.2500000000000000  0.7500000000000000
  0.2500000000000000  0.7500000000000000  0.2500000000000000
  0.7500000000000000  0.7500000000000000  0.2500000000000000
  0.2500000000000000  0.2500000000000000  0.7500000000000000
  0.5000000000000000  0.5000000000000000  0.5000000000000000
  0.5000000000000000  0.0000000000000000 -0.0000000000000000
 -0.0000000000000000  0.5000000000000000 -0.0000000000000000
 -0.0000000000000000  0.0000000000000000  0.5000000000000000
  0.2641862476849527  0.5000000000000000  0.5000000000000000
  0.7358137523150472  0.5000000000000000  0.5000000000000000
  0.5000000000000000  0.2641862476849527  0.5000000000000000
  0.5000000000000000  0.7358137523150472  0.5000000000000000
  0.5000000000000000  0.5000000000000000  0.2641862476849527
  0.5000000000000000  0.5000000000000000  0.7358137523150472
  0.2641862476849527  0.0000000000000000 -0.0000000000000000
  0.7358137523150472  0.0000000000000000  0.0000000000000000
  0.5000000000000000  0.7641862476849528 -0.0000000000000000
  0.5000000000000000  0.2358137523150473  0.0000000000000000
  0.5000000000000000  0.0000000000000000  0.7641862476849528
  0.5000000000000000  0.0000000000000000  0.2358137523150473
  0.7641862476849528  0.5000000000000000 -0.0000000000000000
  0.2358137523150473  0.5000000000000000  0.0000000000000000
 -0.0000000000000000  0.2641862476849527 -0.0000000000000000
 -0.0000000000000000  0.7358137523150472  0.0000000000000000
 -0.0000000000000000  0.5000000000000000  0.7641862476849528
 -0.0000000000000000  0.5000000000000000  0.2358137523150473
  0.7641862476849528  0.0000000000000000  0.5000000000000000
  0.2358137523150473  0.0000000000000000  0.5000000000000000
 -0.0000000000000000  0.7641862476849528  0.5000000000000000
 -0.0000000000000000  0.2358137523150473  0.5000000000000000
 -0.0000000000000000  0.0000000000000000  0.2641862476849527
 -0.0000000000000000  0.0000000000000000  0.7358137523150472
```

POTCAR

copy corresponding psudopotential

KPOINTS

```
Automatic mesh
0                ! number of k-points = 0 -> automatic generation scheme
Gamma            ! generate a Gamma centered grid
4  4  4          ! subdivisions N_1, N_2 and N_3 along recipr. latt. vectors
0. 0. 0.         ! optional shift of the mesh (s_1, s_2, s_3)
```

main output files

OUTCAR

```
   21        1.598   3.560   0.000   5.158
   22        1.598   3.561   0.000   5.158
   23        1.598   3.561   0.000   5.159
   24        1.598   3.562   0.000   5.159
   25        1.598   3.561   0.000   5.159
   26        1.598   3.561   0.000   5.159
   27        1.598   3.560   0.000   5.158
   28        1.598   3.560   0.000   5.158
   29        1.598   3.561   0.000   5.159
   30        1.598   3.561   0.000   5.159
   31        1.598   3.561   0.000   5.159
   32        1.598   3.561   0.000   5.159
   33        1.598   3.560   0.000   5.158
   34        1.598   3.560   0.000   5.158
   35        1.598   3.561   0.000   5.159
   36        1.598   3.561   0.000   5.159
-----------------------------------------------
tot         61.467 147.215   4.627 213.309


 total amount of memory used by VASP MPI-rank0    64392. kBytes
======================================================================

   base      :      30000. kBytes
   nonlr-proj:      14683. kBytes
   fftplans  :       2328. kBytes
   grid      :      11496. kBytes
   one-center:        559. kBytes
   wavefun   :       5326. kBytes


 General timing and accounting informations for this job:
 ========================================================

                  Total CPU time used (sec):      355.847
                            User time (sec):      343.745
                          System time (sec):       12.102
                         Elapsed time (sec):      358.918

                   Maximum memory used (kb):      169288.
                   Average memory used (kb):           0.

                          Minor page faults:      212140
                          Major page faults:         146
                 Voluntary context switches:        6640
```

CONTCAR

```
POSCAR created by SUPERPOSCAR
   10.4200000000000
     1.0000000000000000    0.0000000000000000    0.0000000000000000
     0.0000000000000000    1.0000000000000000    0.0000000000000000
     0.0000000000000000    0.0000000000000000    1.0000000000000000
   Cs   Hf   Cl
     8     4    24
Direct
  0.2537143506843270  0.2500000000000000  0.2500000000000000
  0.7529241775486858  0.7500000000000000  0.7500000000000000
  0.2495692596617585  0.7500000000000000  0.7500000000000000
  0.7516292146652253  0.2500000000000000  0.2500000000000000
  0.7524627549658873  0.2500000000000000  0.7500000000000000
  0.2532846473363009  0.7500000000000000  0.2500000000000000
  0.7524627549658873  0.7500000000000000  0.2500000000000000
  0.2532846473363009  0.2500000000000000  0.7500000000000000
  0.5034600702220177  0.5018239917139182  0.5018239917139182
  0.5034600702220177 -0.0018239917139182 -0.0018239917139182
  0.0022062566256581  0.4993964952200788  0.0006035047799211
  0.0022062566256581  0.0006035047799211  0.4993964952200788
  0.2672226549855391  0.5000069251814556  0.5000069251814556
  0.7393101331842368  0.5044836629050770  0.5044836629050770
  0.5057052624518416  0.2656397851216722  0.5011984603137796
  0.5014036534141956  0.7377645740117785  0.5018983771177175
  0.5057052624518416  0.5011984603137796  0.2656397851216722
  0.5014036534141956  0.5018983771177175  0.7377645740117785
  0.2672226549855391 -0.0000069251814555 -0.0000069251814555
  0.7393101331842368 -0.0044836629050770 -0.0044836629050770
  0.5014036534141956  0.7622354259882215 -0.0018983771177173
  0.5057052624518414  0.2343602148783278 -0.0011984603137798
  0.5014036534141956 -0.0018983771177173  0.7622354259882215
  0.5057052624518414 -0.0011984603137798  0.2343602148783278
  0.7663766002780235  0.4990778752822766  0.0009221247177233
  0.2382296843500349  0.4992828751888567  0.0007171248111433
  0.0023682846084617  0.2632677088250546  0.0006464225526326
  0.0022871479116534  0.7355218910000096  0.0008663697492248
  0.0022871479116534  0.4991336302507751  0.7644781089999904
  0.0023682846084617  0.4993535774473674  0.2367322911749453
  0.7663766002780235  0.0009221247177233  0.4990778752822766
  0.2382296843500349  0.0007171248111433  0.4992828751888567
  0.0022871479116534  0.7644781089999904  0.4991336302507751
  0.0023682846084617  0.2367322911749453  0.4993535774473674
  0.0023682846084617  0.0006464225526326  0.2632677088250546
  0.0022871479116534  0.0008663697492248  0.7355218910000096
```

OSZICAR

```
      N       E                     dE             d eps       ncg     rms          rms(c)
DAV:   1    -0.174854553186E+03    0.14982E-01   -0.96279E+00  2304   0.586E+00    0.443E-01
DAV:   2    -0.174883713334E+03   -0.29160E-01   -0.34334E-01  2880   0.119E+00    0.236E-01
DAV:   3    -0.174882789128E+03    0.92421E-03   -0.62658E-03  2880   0.173E-01    0.165E-01
DAV:   4    -0.174881953492E+03    0.83564E-03   -0.21399E-03  2880   0.919E-02    0.619E-02
DAV:   5    -0.174881881840E+03    0.71652E-04   -0.79365E-04  2880   0.655E-02
  10 F= -.17488188E+03 E0= -.17488188E+03  d E =-.123457E-01
      N       E                     dE             d eps       ncg     rms          rms(c)
DAV:   1    -0.174881848828E+03    0.10466E-03   -0.35256E-03  2880   0.118E-01    0.163E-02
DAV:   2    -0.174881852363E+03   -0.35350E-05   -0.12219E-04  2592   0.268E-02
  11 F= -.17488185E+03 E0= -.17488185E+03  d E =-.123162E-01
      N       E                     dE             d eps       ncg     rms          rms(c)
DAV:   1    -0.174880837456E+03    0.10114E-02   -0.29684E+00  2304   0.318E+00    0.250E-01
DAV:   2    -0.174890133789E+03   -0.92963E-02   -0.10571E-01  2784   0.652E-01    0.122E-01
DAV:   3    -0.174889829956E+03    0.30383E-03   -0.12386E-03  2880   0.814E-02    0.838E-02
DAV:   4    -0.174889617588E+03    0.21237E-03   -0.10399E-03  2832   0.614E-02    0.222E-02
DAV:   5    -0.174889631798E+03   -0.14210E-04   -0.15991E-04  2688   0.243E-02
  12 F= -.17488963E+03 E0= -.17488963E+03  d E =-.777943E-02
      N       E                     dE             d eps       ncg     rms          rms(c)
DAV:   1    -0.174881148715E+03    0.84689E-02   -0.38300E+00  2304   0.361E+00    0.287E-01
DAV:   2    -0.174893181375E+03   -0.12033E-01   -0.13724E-01  2736   0.741E-01    0.139E-01
DAV:   3    -0.174892792090E+03    0.38929E-03   -0.16079E-03  2880   0.929E-02    0.951E-02
DAV:   4    -0.174892519134E+03    0.27296E-03   -0.13548E-03  2928   0.702E-02    0.251E-02
DAV:   5    -0.174892536759E+03   -0.17625E-04   -0.20679E-04  2736   0.279E-02
  13 F= -.17489254E+03 E0= -.17489254E+03  d E =-.106844E-01
      N       E                     dE             d eps       ncg     rms          rms(c)
DAV:   1    -0.174891908235E+03    0.61090E-03   -0.19363E+00  2304   0.255E+00    0.199E-01
DAV:   2    -0.174898118145E+03   -0.62099E-02   -0.69488E-02  2832   0.521E-01    0.103E-01
DAV:   3    -0.174897934605E+03    0.18354E-03   -0.82842E-04  2880   0.653E-02    0.717E-02
DAV:   4    -0.174897784705E+03    0.14990E-03   -0.67757E-04  2880   0.495E-02    0.195E-02
DAV:   5    -0.174897794126E+03   -0.94206E-05   -0.11848E-04  2496   0.217E-02
  14 F= -.17489779E+03 E0= -.17489779E+03  d E =-.525737E-02
      N       E                     dE             d eps       ncg     rms          rms(c)
DAV:   1    -0.174877370822E+03    0.20414E-01   -0.79878E+00  2304   0.519E+00    0.401E-01
DAV:   2    -0.174903065767E+03   -0.25695E-01   -0.28701E-01  2736   0.106E+00    0.209E-01
DAV:   3    -0.174902296479E+03    0.76929E-03   -0.33673E-03  2880   0.133E-01    0.147E-01
DAV:   4    -0.174901644628E+03    0.65185E-03   -0.29683E-03  2880   0.105E-01    0.390E-02
DAV:   5    -0.174901684570E+03   -0.39942E-04   -0.54347E-04  2880   0.459E-02
  15 F= -.17490168E+03 E0= -.17490168E+03  d E =-.914781E-02
      N       E                     dE             d eps       ncg     rms          rms(c)
DAV:   1    -0.174897233722E+03    0.44109E-02   -0.25402E+00  2304   0.300E+00    0.236E-01
DAV:   2    -0.174905322592E+03   -0.80889E-02   -0.94285E-02  2832   0.622E-01    0.124E-01
DAV:   3    -0.174905095338E+03    0.22725E-03   -0.13900E-03  2832   0.830E-02    0.869E-02
DAV:   4    -0.174904903189E+03    0.19215E-03   -0.73173E-04  2880   0.523E-02    0.273E-02
DAV:   5    -0.174904909420E+03   -0.62315E-05   -0.14991E-04  2688   0.265E-02
  16 F= -.17490491E+03 E0= -.17490491E+03  d E =-.322485E-02
```

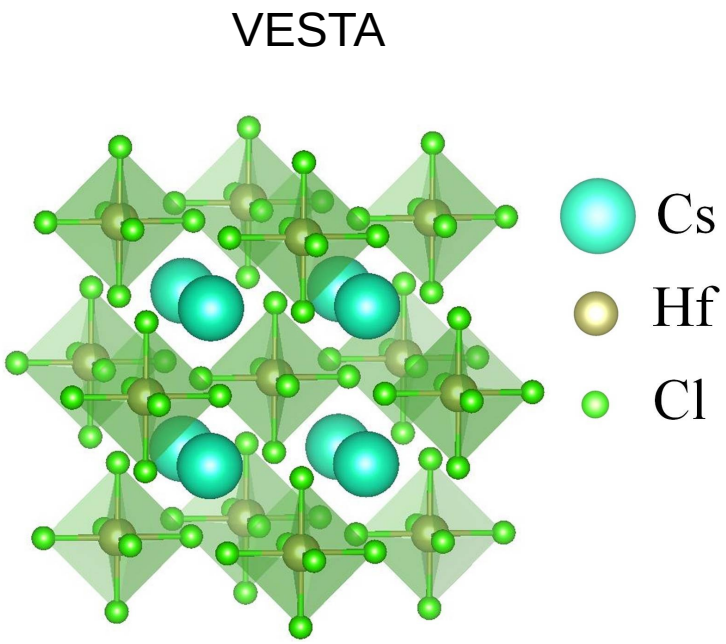
DOSCAR

https://www.vasp.at/vasp-workshop/handsonI.pdf

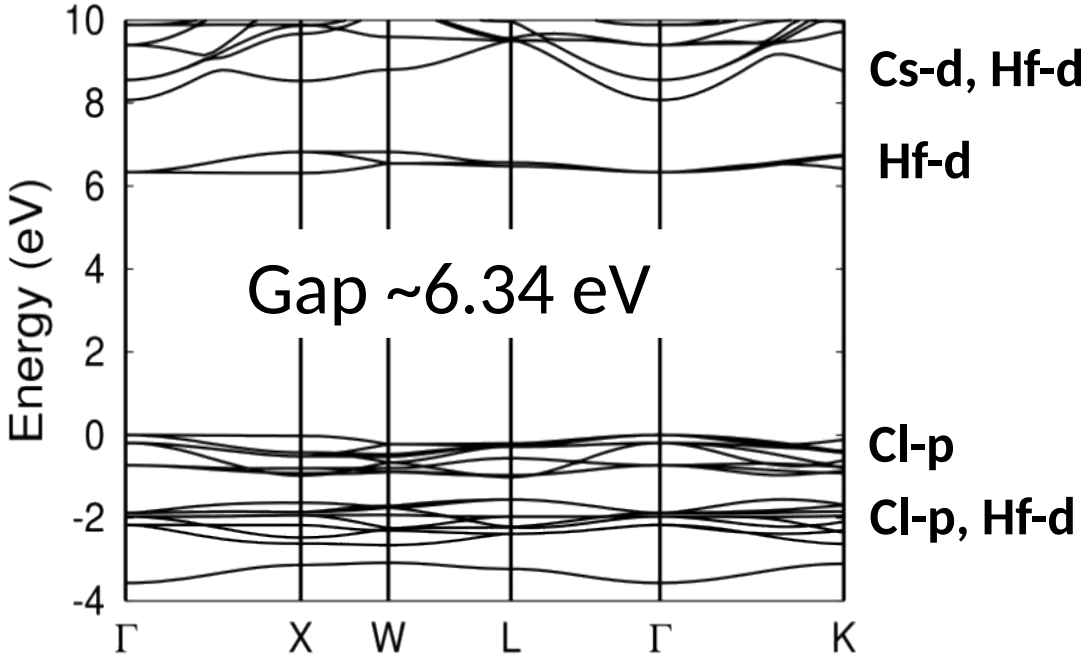
VESTA

vaspkit

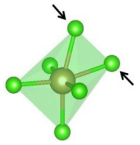
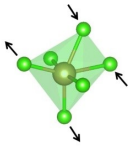
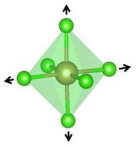
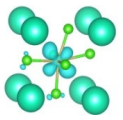
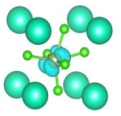
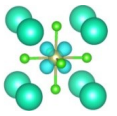
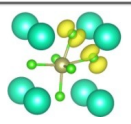
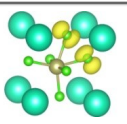
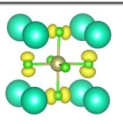
Carrier Self-trapping and Luminescence in Intrinsically Activated Scintillator : Cs_2HfCl_6

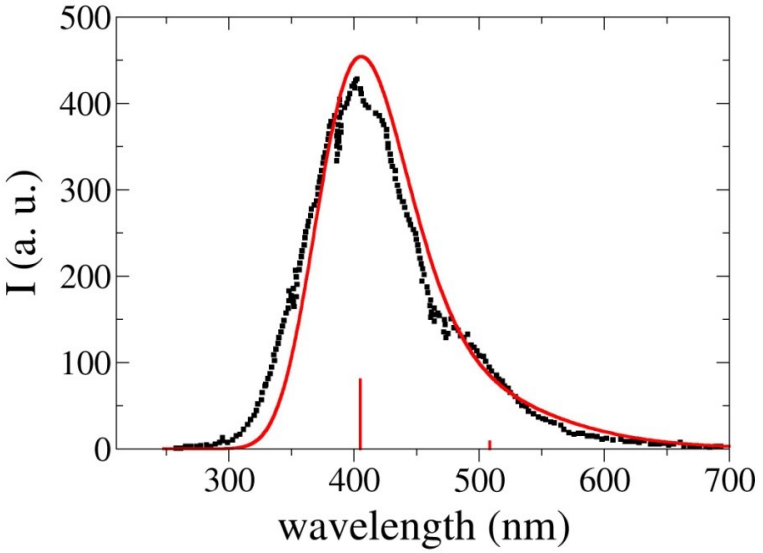


Cubic structure

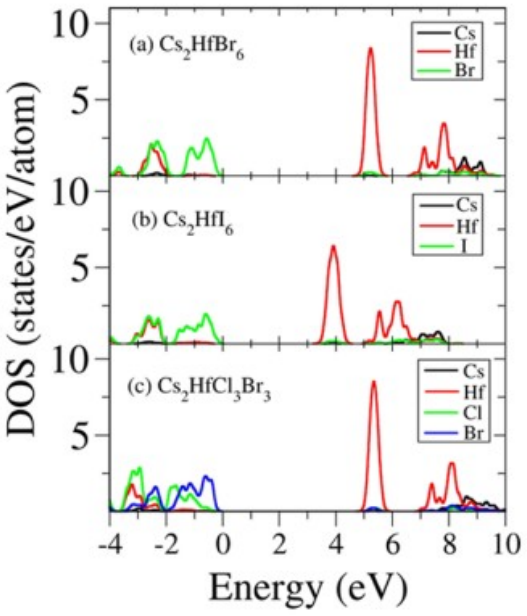


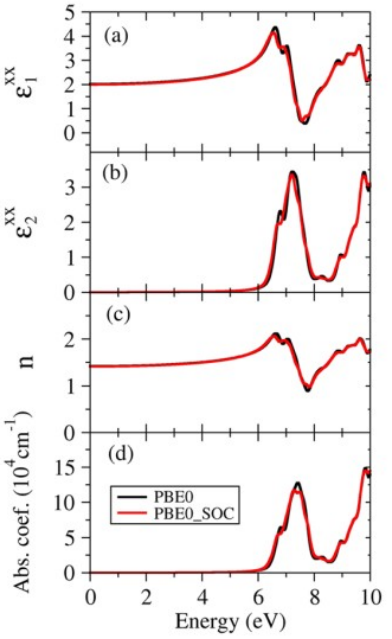
Band structure (PBE0)

		Self-trapped excitons		
		STE1	STE2	STE3
$Cs_8Hf_4Cl_{24}$	Structure			
	Localized electron state			
	Localized hole state			
	BE (eV)	0.45	0.37	0.01
	Emi.(eV)	2.96	3.06	4.97
$Cs_8Hf_3Cl_{24}$:Zr	BE(eV)	0.40	0.36	Unstable
	Emi. (eV)	2.37	2.44	



STE emission ~400


(a) Cs2HfBr6
Cs
Hf
Br
(b) Cs2HfI6
Cs
Hf
I
(c) Cs2HfCl3Br3
Cs
Hf
Cl
Br
DOS (states/eV/atom)
Energy (eV)


(a)
(b)
(c)
(d)
PBE0
PBE0_SOC
Abs. coef. (10^4 cm^-1)
Energy (eV)