Band structure of bulk silicon

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Background

- DFT simulation: Quantum espresso 6.5 version
- Visualize the structure and its k space: XCrySDen

    1. Ubuntu
    2. XCrySDen-1.5.25-bin-semishared
    3. ./xcConfigure

On windows:

1. cygwin 2. DISPLAY=127.0.0.1:0.0; export DISPLAY (add that to your .bash_profile)
3. ./scrysden

Procedure for drawing a band structure

GGA or LDA functionals

perform a single step from superposition of atomic orbitals along the uniform dense k points

create the data to draw the band structure

self-consistent field

pw.x

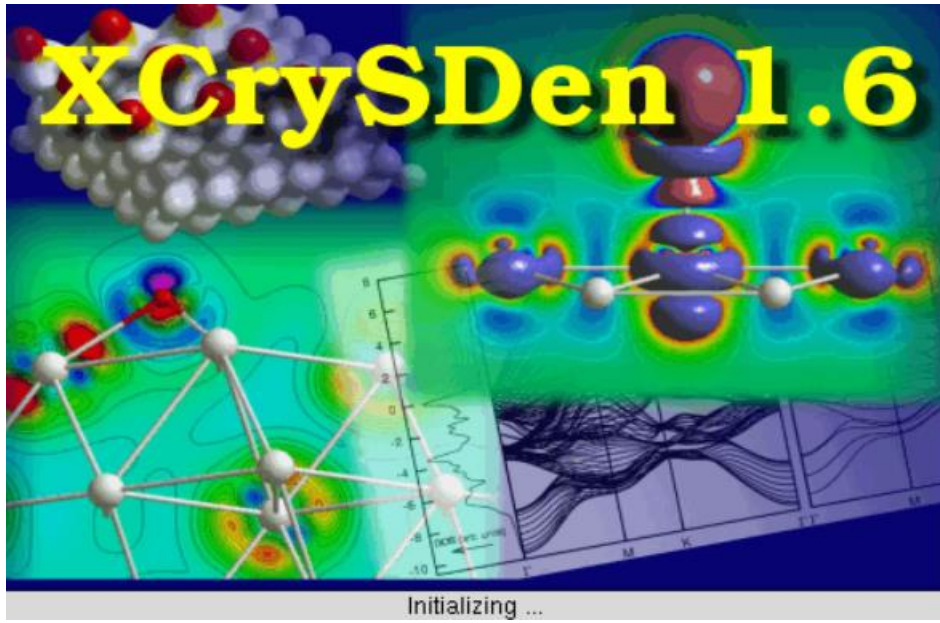
pw.x (nscf) → pw.x (bands) → band.x->plotband.x

pw.x (bands)

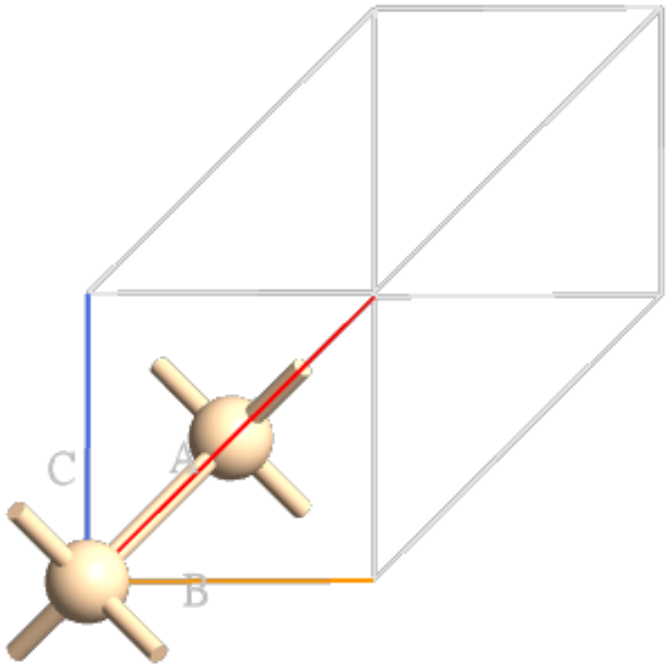
perform a band structure calculation along the given k-path

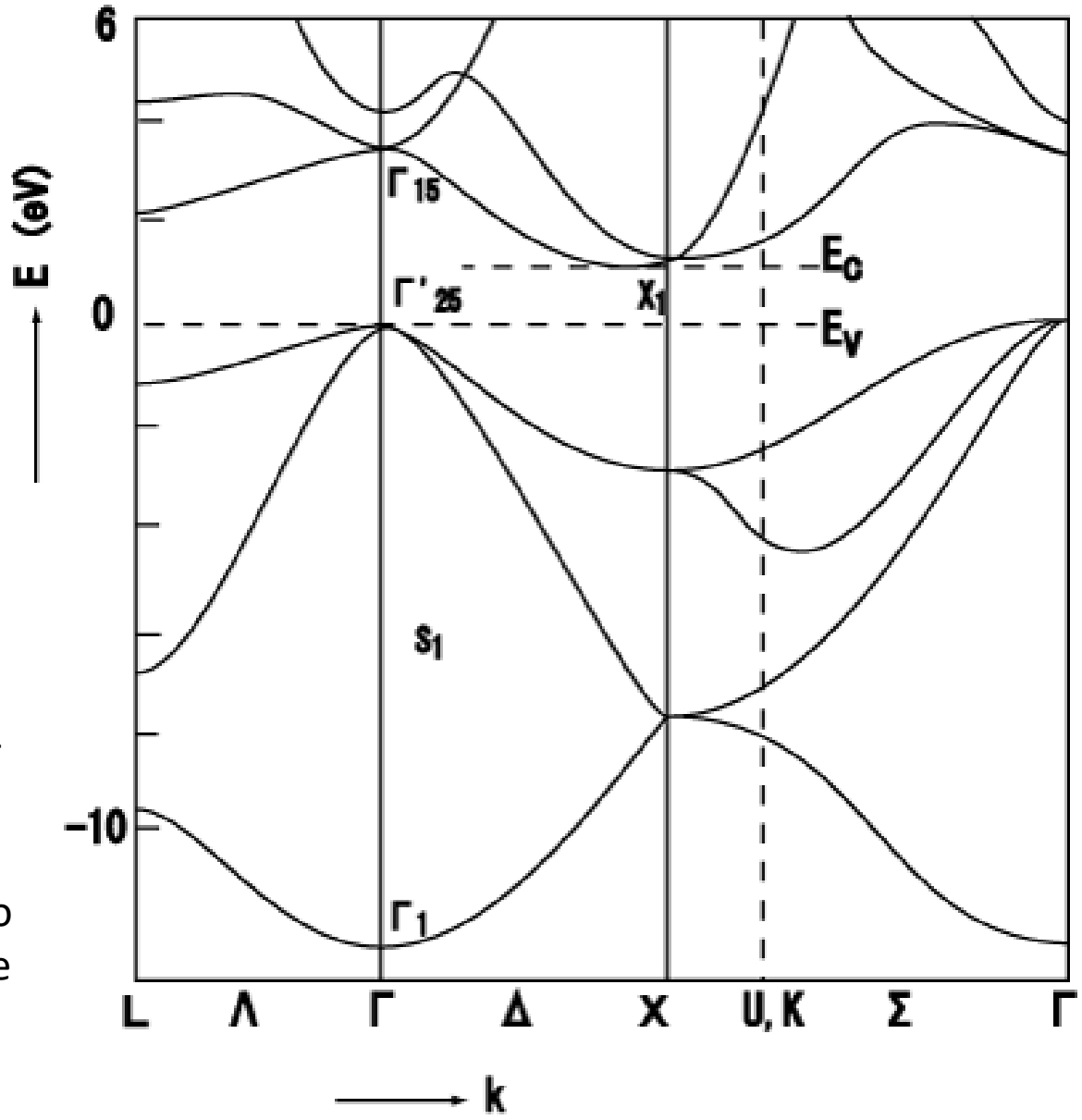
```
5
  0.0000 0.5000 0.0000 20 !L
  0.0000 0.0000 0.0000 30 !Gamma
  -0.500 0.0000 -0.500 10 !X
  -0.375 0.2500 -0.375 30 !U
  0.0000 0.0000 0.0000 20 !Gamma
```

K-points generation



Bulk Silicon





Bulk silicon has an indirect bandgap of 1.1 eV,

1. limits its photon absorption capacity to the visible and near infrared (IR) region of the electromagnetic spectrum
2. Silicon solar cells have been the dominant driving force in photovoltaic technology for the past several decades due to the relative abundance and environmentally friendly nature of silicon.

Silicon input file (1)

1. first compute the self-consistent-calculation

```
&control
 calculation='scf',
 prefix='si',
 pseudo_dir= '/research/lens/pseudo/',
 outdir = '/scratch/cyulu/',
/
&system
    ibrav=2, celldm(1) =10.410909236,
    nat=2, ntyp=1,
    ecutwfc=40
    ecutrho=320
    nbnd=8
    !occupations='smearing', smearing='gaussian',degauss=0.005
/
&electrons
 conv_thr=1.d-10,
/
ATOMIC_SPECIES
Si  28.0855  Si.pbe-nl-rrkjus_psl.1.0.0.UPF
ATOMIC_POSITIONS {crystal}
Si  -0.25   0.75   -0.25
Si   0.00   0.00    0.00
K_POINTS {automatic}
 8 8 8 0 0 0
```

Pesudopotential suggest:
UPSS= Ecutrho ~8*ecutwfc

At least more than 4 because Valence band has only 4 nbnd, and we want to know some information for the conduction band

Silicon input file (2)

1. first compute the self-consistent-calculation

```
&control
 calculation='scf',
 prefix='si',
 pseudo_dir= '/research/lens/pseudo/',
 outdir = '/scratch/cyulu/',
/
&system
    ibrav=2, celldm(1) =10.410909236,
    nat=2, ntyp=1,
    ecutwfc=40
    ecutrho=320
    nbnd=8
    !occupations='smearing', smearing='gaussiar
/
&electrons
 conv_thr=1.d-10,
/
ATOMIC_SPECIES
Si  28.0855  Si.pbe-nl-rrkjus_psl.1.0.0.UPF
ATOMIC_POSITIONS {crystal}
Si  -0.25   0.75   -0.25
Si   0.00   0.00    0.00
K_POINTS {automatic}
 8 8 8 0 0 0
```

```
<UPF version="2.0.1">
  <PP_INFO>
Generated using "atomic" code by A. Dal Corso  v.6.3
Author: ADC
Generation date:  4Sep2018
Pseudopotential type: USPP
Element: Si
Functional: PBE
    Suggested minimum cutoff for wavefunctions:  44. Ry
    Suggested minimum cutoff for charge density: 175. Ry
    The Pseudo was generated with a Scalar-Relativistic Calculation
    L component and cutoff radius for Local Potential:  2   1.7000
    Pseudopotential contains additional information for GIPAW reconstruction.
    Valence configuration:
    nl pn  l   occ       Rcut     Rcut US       E pseu
    3S  1  0  2.00      1.600      1.800    -0.794728
    3P  2  1  2.00      1.600      1.800    -0.299965
    Generation configuration:
    3S  1  0  2.00      1.600      1.800    -0.794725
    3S  1  0  0.00      1.600      1.800     6.000000
    3P  2  1  2.00      1.600      1.800    -0.299965
    3P  2  1  0.00      1.600      1.800     6.000000
    3D  3  2  0.00      1.700      1.700     0.100000
    Pseudization used: troullier-martins
functional="PBE" z_valence="4.000000000000e0"
```

4 electron per silicon atom during the calculation

Details can be found in https://www.quantum-espresso.org/pseudopotentials/unified-pseudopotential-format

Silicon band structure: scf output


```
! occupations='smearing', smearing='gaussian',degauss=0.005
```

No smearing

smearing

```
        k =-0.5000-1.0000 0.0000 (  1216 PWs)   bands (ev):

   -1.7749  -1.7749   2.0882   2.0882  10.0384  10.0384  10.6114  10.6114

    highest occupied, lowest unoccupied level (ev):     5.7619    6.4470

!    total energy              =     -22.83945479 Ry
     Harris-Foulkes estimate   =     -22.83945479 Ry
     estimated scf accuracy    <          4.8E-11 Ry
```

```
        k =-0.5000-1.0000 0.0000 (  1216 PWs)   bands (ev):

   -1.7749  -1.7749   2.0882   2.0882  10.0384  10.0384  10.6114  10.6114

    the Fermi energy is     6.1500 ev

!    total energy              =     -22.83945479 Ry
     Harris-Foulkes estimate   =     -22.83945479 Ry
     estimated scf accuracy    <          4.8E-11 Ry
```

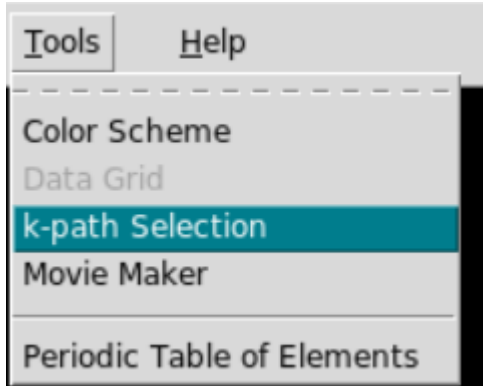
Explanation:

1. In a semiconductor, if we have a system with 8 electrons, then at every k-point the first 4 doubly occupied states will be populated.
2. In a metal, whether or not a state is occupied depends on its energy and the value of the Fermi level.

Silicon band structure: pw.x

1. A detailed k path is required for Bands.x input file, which is basically same as the scf input file, except a detailed k path.

```
K_POINTS {crystal_b}
5
  0.0000 0.5000 0.0000 20 !L
  0.0000 0.0000 0.0000 30 !Gamma
  -0.500 0.0000 -0.500 10 !X
  -0.375 0.2500 -0.375 30 !U
  0.0000 0.0000 0.0000 20 !Gamma
```




```
#
# #---------------------------------#
# # REAL FORM of k-point COORDINATES #
# #---------------------------------#
#

Real form of k-point coordinates (kx,ky,kz,label):
   0.5000000000     0.5000000000     0.5000000000     L
   0.0000000000     0.0000000000     0.0000000000     GAMMA
   0.5000000000     0.5000000000     0.0000000000     X
   0.6250000000     0.6250000000     0.2500000000     U
   0.0000000000     0.0000000000     0.0000000000     GAMMA
```

Procedure for drawing a band structure

GGA or LDA functionals

perform a single step from superposition of atomic orbitals along the uniform dense k points

create the data to draw the band structure

self-consistent field

pw.x (nscf) → pw.x (bands) → band.x->plotband.x

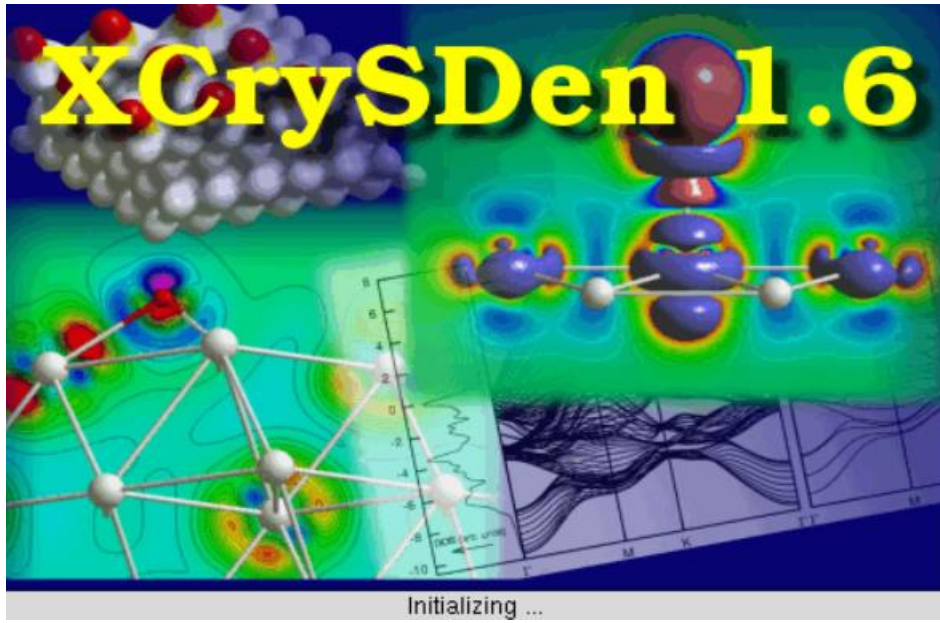
pw.x

pw.x (bands)

perform a band structure calculation along the given k-path

```
5
  0.0000 0.5000 0.0000 20 !L
  0.0000 0.0000 0.0000 30 !Gamma
  -0.500 0.0000 -0.500 10 !X
  -0.375 0.2500 -0.375 30 !U
  0.0000 0.0000 0.0000 20 !Gamma
```

K-points generation



Silicon band structure: bands.x

1. Arrange the plot file for band structure;

```
&bands
  outdir='/scratch/cyulu/'
  prefix='si'
  filband='si.bands.dat'
/
```

- Input file for plotbands.x

```
1 si.bands.dat
2 -7 16
3 si.bands.xmgr
4 si.bands.ps
5 6.1330
6 2 6.1330
7
```

→ Emin, Emax

→ !output for xmgrace plotting

→ Fermi energy

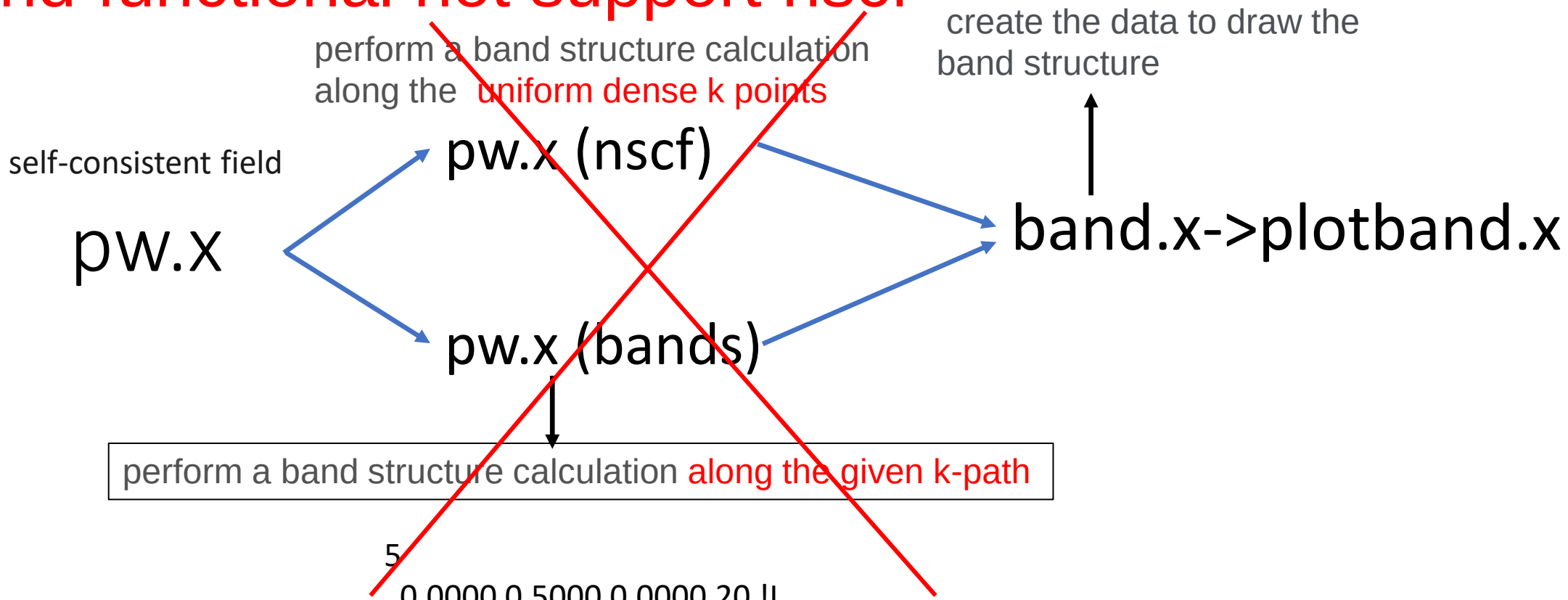
→ ! The Estep and Reference Energy

Backup

Procedure for drawing a band structure

- GGA or LDA Hybrid functionals:

  hybrid functional not support nscf



Silicon band structure: hybrid functionals: HSE

Silicon band structure: hybrid functionals: HSE

1. (hybrid functional) HSE Si band gap

```
input_dft='HSE',
nqx1=1, nqx2=1, nqx3=1,
x_gamma_extrapolation=.true.,
exxdiv_treatment='gygi-baldereschi',
```

gygi-baldereschi:

The q+G=0 divergence

- Gygi-Baldereschi PRB 34, 4405 (1986)

$$\rho^{\mathbf{k}-\mathbf{q},v'}_{\mathbf{k},v}(\mathbf{r}) = \phi^*_{\mathbf{k}-\mathbf{q},v'}(\mathbf{r})\phi_{\mathbf{k},v}(\mathbf{r}) \quad \Longrightarrow \quad A(\mathbf{q}+\mathbf{G}) = \frac{\Omega}{(2\pi)^3}\int d\mathbf{k}\ \ |\rho^{\mathbf{k}-\mathbf{q},v'}_{\mathbf{k},v}(\mathbf{q}+\mathbf{G})|^2$$

$$= \frac{1}{N_\mathbf{k}}\sum_\mathbf{k} |\rho^{\mathbf{k}-\mathbf{q},v'}_{\mathbf{k},v}(\mathbf{q}+\mathbf{G})|^2$$

$$E_{HF} = -\frac{4\pi e^2}{2\Omega} \times \frac{\Omega}{(2\pi)^3}\int d\mathbf{q}\sum_\mathbf{G}\frac{A(\mathbf{q}+\mathbf{G})}{|\mathbf{q}+\mathbf{G}|^2}$$

integrable divergence

Procedure for drawing a HSE bandstructure

- Hybrid functional

create all the files you need to plot your band structure

pw.x ->open_grid.x->band.x->plotband.x

awk '/wannier90/{flag=1;next}/OPEN_GRID :/{flag=0}flag' opengrid.out >kpoints.dat

--writes Kohn-Sham orbitals for the complete k-point grid (not symmetry independent points only) in real space. Useful for further processing. It can be used to generate the Kohn-Sham state data required in pw2wannier.x and Wannier90 from the initial SCF calculation, bypassing the non-SCF calculation step.

```
5
 0.0000 0.5000 0.0000 20 !L
 0.0000 0.0000 0.0000 30 !Gamma
 -0.500 0.0000 -0.500 10 !X
 -0.375 0.2500 -0.375 30 !U
 0.0000 0.0000 0.0000 20 !Gamma
```