Band structure calculation using KKR-Green's function method

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1 Introduction

In this document, how to use Machikaneyama2002 (AkaiKKR), a KKR-CPA-LDA package, is briefly guided. The KKR method is one of the methods of electronic structure calculation and is also called"Green's function method." KKR indicates the initials of Korringa, Kohn, and Rostoker, who invented this method. CPA means the coherent potential approximation, which can deal with random systems. Green's function might be difficult to understand if you are trained with ordinary band structure calculations, which solve an eigenvalue problem by diagonalization. However, you can apply KKR-CPA to much wider range of situation than ordinary band structure calculations can do. For example, it can deal with finite temperature magnetism and partial disorder systems since CPA can treat not only periodic systems but also random systems.

2 Get started

The KKR band structure code has been developed by H. Akai since 1979. The KKR package is a set of subroutines written in FORTRAN77. It is not so difficult for you to perform some small calculations using this package even if you are not familiar with the computational physics and numerical techniques used in the method.

2.1 Get the program

Usually, the downloaded KKR program package is archived and compressed. Thus compressed file is named as 'cpa2002v00x.tar.gz'. First you put 'cpa2002v00x.tar.gz' under your home directly. Next, you must decompress it and get the original form. The following commands should be executed.

```
~> tar xvfz cpa2002v00x.tar.gz
```

Now, you find the following files in the directory, /cpa2002v00x/.

```
~>cd cpa2002v00x
~/cpa2002v00x>ls
data            gpdos.f         makefile        source
gpd             in              readme          util
```

Here, the file 'makefile' is used to compile the sources. New directories, 'source', 'in', 'out' and 'data', are created. Under the directory 'source' you find all of the source codes, and 'in', 'out' and 'data' may be used to save input, output and data files, respectively. You can delete 'cpa2002v00x.tar.gz' which is not needed anymore.

2.2 Compile the program

Since the package contains many subroutines, it is convenient to use the 'make' command. The 'make' command refers to the 'makefile' and compiles the files whose names are written in the 'makefile'. Moreover, the 'make' command finds out the files that have been modified since the last time, and compiles those files.

```
^/cpa2002v00x> make
```

Just key in, and you will get an executable file 'specx'.

2.3 Execute the program

To start a calculation, an input file in which lattice parameters and some numerical parameters are written is needed. How to write the input file is explained in the next section. If you want to execute a KKR calculation with your input file 'input' and save a result in a file 'output', key in the following.

```
~/cpa2002v006x> specx < in/input > out/output &
```

The last character '&' means that this job should be carried out as a background job.

3 Execution of the calculation

3.1 Input File

The lattice parameters, such as the Bravais type, the lattice constants and atomic numbers, and so on, are written in an input file and it is read in by the program when the kkr is executed. As an example, the input file used in the calculation of fcc NiFe alloy is the following.

```
c----------------------- input data -------------------------
c   go     file
    go     data/feni
c -----------------------------------------------------------
c   brvtyp     a      c/a   b/a  alpha  beta  gamma
     bcc     5.3056 ,     ,     ,     ,     ,     ,
c -----------------------------------------------------------
c   edelt    ewidth   reltyp   sdftyp   magtyp   record
    0.001     1.2      nrl      mjw      mag      init
c -----------------------------------------------------------
c   outtyp   bzqlty   maxitr   pmix
    update     4        80    0.024
c -----------------------------------------------------------
c   ntyp
     1
c -----------------------------------------------------------
c   type   ncmp   rmt   field   l_max   anclr   conc
    FeNi     2     0      0       2       26      60
                                         28      40
c -----------------------------------------------------------
c   natm
     1
c -----------------------------------------------------------
c   atmicx                              atmtyp
     0           0           0           FeNi
c -----------------------------------------------------------
```

The lines which begin with the letter 'c' is neglected. Names of the fields are also commented in the sample input file. The delimiter is a space ' ' or a comma ','. In table 1, what is written in each field is summarized.

In the following, some comments and notes are given.

- [go] In '**dsp**' and '**dos**' modes, values of record, outtyp and maxitr are automatically set to be '**2nd**', '**quit**' and '**1**', respectively.

Table 1: Parameters written in the input file.

Field	Value	Meaning
go	go	perform a band structure calculation.
	dos	calculate a density of states.
	dsp	display a previous result.
	spc	calculate Bloch spectral function (dispersion relation).
file	*file name*	file name in which a potential data is written.
brvtyp		which type of the Bravais lattices.
	fcc	face centered cubic
	bcc	body centered cubic
	hcp(hex)	hexagonal close packed
	sc	simple cubic
	bct	body centered tetragonal
	st	simple tetragonal
	fco	face centered orthorhombic
	bco	body centered orthorhombic
	bso	base centered orthorhombic
	so	simple orthorhombic
	bsm	base centered monoclinic
	sm	simple monoclinic
	trc	triclinic
	rhb(trg)	rhombohedral (trigonal)
	fct	face centered tetragonal
a		lattice constant in atomic unit.
c/a		c/a ratios of lattice constants.
b/a		b/a ratios of lattice constants.
alpha		α in degrees.
beta		β in degrees.
gamma		γ in degrees.
edelt	∼0.001	Imaginary part at the Fermi level in Ry (see Fig. 1).
ewidth	—	Width of the energy contour in Ry (see Fig. 1).
reltyp	nrl	no relativistic treatment.
	sra	scaler relativistic approximation.
sdftyp	mjw, vbh, vwn	which exchange correlation potential is used.
magtyp	mag	magnetic.
	nmag	non-magnetic.
	-mag(rvrs)	change the sign of the magnetization.
	kick	transfer to the magnetic state artificially.
record	init	initially start a calculation.
	2nd	continues the last calculation.
	1st	continues the second last calculation.
outtyp	update	potential data is updated.
	quit	potential data is not updated.
bzqlty	0, 1, 2,...	The bigger, the finer mesh in the Brillouin zone.
	t, s, m, l, h, u	see nfqlty.f
maxitr		the maximum number of the iteration loop.
pmix	0.01-0.03	a parameter used in mixing V^{in} and V^{out}.
ntyp		how many types of atom exist in a unit cell.
type	*type name*	names of the respective types of site.
ncmp		how many components exist in the site.
rmt		muffin tin radius in a.
field		external magnetic field at each site in Ry.
l_max		the maximum angular momentum taken into account.
anclr		atomic number.
conc		concentration of the components at the site.
natm		number of atoms in a unit cell.
atmicx	*coordinates*	where each atom is (in a).
atmtyp	*type name*	which type of the site at the lattice point.

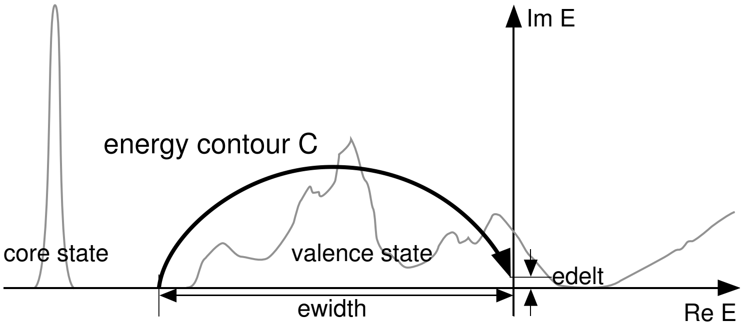

Figure 1: The energy contour.

- **[file]** You can specify a file name of a potential data using a relative pass.
- **[brvtyp]** If c/a, b/a, α, β and γ are evident from '**brvtyp**' , you can omit to write them.
- **[record]** The previous potential data is stored together with the latest potential data in the data, in case that the latest calculation terns out rubbish. '**2nd**' means that the calculation starts with the latest data file, and '**1st**' means that the calculation starts with the data of the last but one.
- **[rmt]** If the muffin-tin spheres whose radii are given by '**rmt**' conflict each other their radii are reduced. If '**rmt**' = 0, muffin tin radii are set so that their ratio is equal to the ratio of the atomic radii.
- **[anclr]** 'anclr'=0 means that a vacancy is put on the lattice point.
- **[conc]** Concentrations are normalized in each site. It is not necessary that the sum of them equal to 1.
- **[atmicx]** The lattice point at which an atom is put is specified with the Cartesian coordinate (*e.g.*, written as 0.5, 0.5, 0.5) or with the primitive vector (*e.g.*, written as 0.5a, 0.5b, 0.5c). They can have a fractional form such as 1/3, 2/3a, and 1d0/3d0x.
- If the input data for several different systems are contained in a single file, they are performed sequentially.

3.2 Output File

A result of a calculation is shown on a display or is redirected to an output file. As an example, the output of the calculation for NiFe alloy is shown, for which the input file has already been shown.

```
 2-Feb-2005
   meshr  mse    ng     mxl
     400     35     15      3

  data read in
  go=go   file=data/feni
  brvtyp=bcc  a=  5.30560  c/a=1.00000  b/a=1.00000
  alpha=  0.0  beta=  0.0  gamma=  0.0
  edelt= 0.0010  ewidth=  1.200  reltyp=nrl    sdftyp=mjw        magtyp=mag
  record=init  outtyp=update  bzqlty=4   maxitr= 80  pmix=0.02400
  ntyp= 1  natm= 1  ncmpx= 2

  complex energy mesh
  1( -1.2000, 0.0000)   2( -1.1998, 0.0030)   3( -1.1990, 0.0070)
  4( -1.1970, 0.0121)   5( -1.1928, 0.0186)   6( -1.1849, 0.0267)
  7( -1.1710, 0.0368)   8( -1.1478, 0.0489)   9( -1.1111, 0.0629)
 10( -1.0562, 0.0779)  11( -0.9792, 0.0930)  12( -0.8787, 0.1063)
```

```
 13( -0.7577, 0.1158)  14( -0.6240, 0.1199)  15( -0.4891, 0.1179)
 16( -0.3646, 0.1104)  17( -0.2591, 0.0988)  18( -0.1764, 0.0850)
 19( -0.1156, 0.0708)  20( -0.0735, 0.0575)  21( -0.0455, 0.0458)
 22( -0.0276, 0.0360)  23( -0.0165, 0.0280)  24( -0.0098, 0.0216)
 25( -0.0057, 0.0165)  26( -0.0033, 0.0126)  27( -0.0019, 0.0096)
 28( -0.0011, 0.0073)  29( -0.0006, 0.0055)  30( -0.0004, 0.0042)
 31( -0.0002, 0.0032)  32( -0.0001, 0.0024)  33( -0.0001, 0.0018)
 34(  0.0000, 0.0014)  35(  0.0000, 0.0010)

  file to be accessed=data/feni
  created

  lattice constant
  bravais=bcc   a=  5.30560   c/a=1.0000   b/a=1.0000
  alpha=  90.00   beta=  90.00   gamma=  90.00

  primitive translation vectors
  a=( -0.50000  0.50000  0.50000)
  b=(  0.50000 -0.50000  0.50000)
  c=(  0.50000  0.50000 -0.50000)

  type of site
  type=FeNi      rmt=0.43301  field=  0.000   lmxtyp=  2
                 component= 1  anclr=  26.  conc= 0.6000
                 component= 2  anclr=  28.  conc= 0.4000

  atoms in the unit cell
  position=   0.00000000   0.00000000   0.00000000  type=FeNi

***msg in spmain...new ew, ez generated
  ew=   0.09998  ez=   0.80300

  preta= 0.35542  eta= 0.35542
  isymop= 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1

  last= 243   np= 15   nt= 141   nrpt= 169   nk=   29   nd=   1

  itr=  1      rms error = -1.872
  itr=  2      rms error = -2.390
  itr=  3      rms error = -2.879
  itr=  4      rms error = -3.357
  itr=  5      rms error = -3.890
  itr=  6      rms error = -3.879
  itr=  7      rms error = -4.878
  itr=  8      rms error = -4.850
  itr=  9      rms error = -5.574
  itr= 10      rms error = -6.235
  interval= 10     cpu time=      0.00 sec

        nl      cnf         energy
   -----------------------------------
        1s     2.000       -508.5203
        2s     2.000        -59.2074
        2p     6.000        -51.1806
        3s     2.000         -6.8027
        3p     6.000         -4.4563
        3d     6.000         -0.6696
        4s     2.000         -0.4930

  itr=  1      rms error = -1.724
  itr=  2      rms error = -2.239
  itr=  3      rms error = -2.657
  itr=  4      rms error = -2.967
  itr=  5      rms error = -3.645
  itr=  6      rms error = -3.695
  itr=  7      rms error = -4.268
  itr=  8      rms error = -5.061
  itr=  9      rms error = -5.356
  itr= 10      rms error = -5.470
  itr= 11      rms error = -6.321
  interval= 11     cpu time=      0.01 sec

        nl      cnf         energy
   -----------------------------------
```

```
      1s     2.000       -595.8142
      2s     2.000        -70.7050
      2p     6.000        -61.8163
      3s     2.000         -7.9863
      3p     6.000         -5.2730
      3d     8.000         -0.7806
      4s     2.000         -0.5252

record 1 will be overlaied by input and
record 2 will be replaced by new output.

core configuration for Z= 26
state  1s 2s 2p 3s 3p 3d 4s 4p 4d 5s 5p 4f 5d 6s 6p 5f 6d 7s
 up     1  1  3  1  3  0  0  0  0  0  0  0  0  0  0  0  0  0
down    1  1  3  1  3  0  0  0  0  0  0  0  0  0  0  0  0  0

core configuration for Z= 28
state  1s 2s 2p 3s 3p 3d 4s 4p 4d 5s 5p 4f 5d 6s 6p 5f 6d 7s
 up     1  1  3  1  3  0  0  0  0  0  0  0  0  0  0  0  0  0
down    1  1  3  1  3  0  0  0  0  0  0  0  0  0  0  0  0  0

***** self-consistent iteration starts *****
   FeNi
itr=  1 neu= -1.4601  moment=  0.0905  te=  -2718.3225808  err=  0.119
itr=  2 neu= -0.8991  moment=  0.1151  te=  -2718.3221114  err= -0.277
itr=  3 neu= -0.2974  moment=  0.1168  te=  -2718.3157206  err= -0.149
itr=  4 neu=  0.1787  moment=  0.1296  te=  -2718.3197036  err= -0.627
itr=  5 neu=  0.5050  moment=  0.1933  te=  -2718.3214574  err= -0.407
itr=  6 neu=  0.6526  moment=  0.2873  te=  -2718.3261849  err= -0.483
itr=  7 neu=  0.5415  moment=  0.4203  te=  -2718.3258145  err= -0.530
itr=  8 neu=  0.3129  moment=  0.5384  te=  -2718.3258235  err= -1.056
itr=  9 neu=  0.1143  moment=  0.7051  te=  -2718.3265769  err= -0.801
itr= 10 neu= -0.0203  moment=  0.8951  te=  -2718.3295190  err= -0.873
itr= 11 neu= -0.1221  moment=  1.0540  te=  -2718.3323905  err= -0.967
itr= 12 neu= -0.1746  moment=  1.2526  te=  -2718.3352375  err= -0.844
itr= 13 neu= -0.1626  moment=  1.4605  te=  -2718.3369449  err= -0.608
itr= 14 neu= -0.1454  moment=  1.6426  te=  -2718.3395758  err= -0.754
itr= 15 neu= -0.1518  moment=  1.6880  te=  -2718.3406928  err= -0.650
itr= 16 neu= -0.1663  moment=  1.7401  te=  -2718.3410295  err= -0.607
itr= 17 neu= -0.1522  moment=  1.7988  te=  -2718.3415185  err= -1.255
itr= 18 neu= -0.1303  moment=  1.7861  te=  -2718.3414079  err= -1.326
itr= 19 neu= -0.0791  moment=  1.7878  te=  -2718.3410749  err= -1.206
itr= 20 neu= -0.0246  moment=  1.7774  te=  -2718.3410051  err= -1.553
itr= 21 neu=  0.0213  moment=  1.7734  te=  -2718.3409834  err= -1.224
itr= 22 neu=  0.0494  moment=  1.7695  te=  -2718.3410544  err= -1.282
itr= 23 neu=  0.0583  moment=  1.7667  te=  -2718.3410975  err= -1.829
itr= 24 neu=  0.0518  moment=  1.7646  te=  -2718.3410481  err= -1.769
itr= 25 neu=  0.0361  moment=  1.7609  te=  -2718.3409914  err= -1.879
itr= 26 neu=  0.0172  moment=  1.7587  te=  -2718.3409593  err= -2.014
itr= 27 neu=  0.0005  moment=  1.7597  te=  -2718.3409526  err= -1.849
itr= 28 neu= -0.0111  moment=  1.7612  te=  -2718.3409625  err= -2.108
itr= 29 neu= -0.0169  moment=  1.7625  te=  -2718.3409716  err= -2.097
itr= 30 neu= -0.0176  moment=  1.7634  te=  -2718.3409749  err= -2.114
itr= 31 neu= -0.0147  moment=  1.7639  te=  -2718.3409743  err= -2.287
itr= 32 neu= -0.0102  moment=  1.7640  te=  -2718.3409723  err= -2.403
itr= 33 neu= -0.0055  moment=  1.7640  te=  -2718.3409707  err= -2.315
itr= 34 neu= -0.0017  moment=  1.7638  te=  -2718.3409703  err= -2.499
itr= 35 neu=  0.0009  moment=  1.7637  te=  -2718.3409703  err= -2.727
itr= 36 neu=  0.0024  moment=  1.7635  te=  -2718.3409704  err= -2.832
itr= 37 neu=  0.0029  moment=  1.7633  te=  -2718.3409703  err= -2.844
itr= 38 neu=  0.0026  moment=  1.7632  te=  -2718.3409701  err= -2.749
itr= 39 neu=  0.0019  moment=  1.7631  te=  -2718.3409699  err= -2.813
itr= 40 neu=  0.0010  moment=  1.7631  te=  -2718.3409698  err= -2.999
itr= 41 neu=  0.0002  moment=  1.7631  te=  -2718.3409698  err= -3.004
interval= 41     cpu time=     17.79 sec
sdftyp=mjw     reltyp=nrl     dmpc=0.024
   FeNi
itr= 41  neu  0.0002  chr,spn  8.8000  1.7631  intc,ints  0.9632 -0.0234
rms err= -3.164 -3.274 -3.004 -3.177
ef=   0.7260630   0.7343370  def=   2.6962356  12.2016065
total energy=  -2718.3409698
```

```
                           *** type-FeNi     Fe (z= 26.0) ***
  core charge in the muffin-tin sphere =17.9787766
  valence charge in the cell (spin up  ) =     0.19826(s)   0.19326(p)   4.36075(d)
  valence charge in the cell (spin down) =     0.19758(s)   0.20985(p)   1.84235(d)
  total charge=  24.98082   valence charge (up/down)=   4.75227   2.24978
  spin moment=   2.50249  orbital moment=   0.00000

  core level  (spin up  )
     -507.1266873 Ry(1s)       -57.8685202 Ry(2s)       -49.8296484 Ry(2p)
       -5.5302084 Ry(3s)        -3.1878588 Ry(3p)
  core level  (spin down)
     -507.1176964 Ry(1s)       -57.7567489 Ry(2s)       -49.7425563 Ry(2p)
       -5.3171341 Ry(3s)        -2.9808461 Ry(3p)

  hyperfine field of FeNi
    -239.803 KG (core=  -250.980 KG  valence=    11.177 KG )
  core contribution
    -21.109 KG(1s)    -548.149 KG(2s)     318.277 KG(3s)

  charge density at the nucleus
      11820.1880 (core=    11814.5387  valence=        5.6493 )
  core contribution
      10701.4478(1s)         972.7303(2s)         140.3607(3s)


                           *** type-FeNi     Ni (z= 28.0) ***
  core charge in the muffin-tin sphere =17.9914848
  valence charge in the cell (spin up  ) =     0.21450(s)   0.20389(p)   4.50139(d)
  valence charge in the cell (spin down) =     0.22638(s)   0.23660(p)   3.74662(d)
  total charge=  27.12086   valence charge (up/down)=   4.91978   4.20959
  spin moment=   0.71019  orbital moment=   0.00000

  core level  (spin up  )
     -594.3771108 Ry(1s)       -69.2884479 Ry(2s)       -60.3956628 Ry(2p)
       -6.5907736 Ry(3s)        -3.8813868 Ry(3p)
  core level  (spin down)
     -594.3686783 Ry(1s)       -69.2422357 Ry(2s)       -60.3587004 Ry(2p)
       -6.5162732 Ry(3s)        -3.8088998 Ry(3p)

  hyperfine field of FeNi
    -166.611 KG (core=   -77.215 KG  valence=   -89.396 KG )
  core contribution
     -9.105 KG(1s)    -204.777 KG(2s)     136.667 KG(3s)

  charge density at the nucleus
      14827.9567 (core=    14822.0421  valence=        5.9145 )
  core contribution
      13396.9377(1s)        1243.1999(2s)         181.9046(3s)


 cpu used        17.94 sec
```

First, a date, 'meshr', 'mse', 'ng' and 'mxl' are output. The next block shows meshes on an energy contour and the contents of the input file. If muffin-tin radii are modified, the new radii are shown. The next information shows how many lattice points (nrpt), reciprocal lattice points (ngpt) and k-points (nk) are needed. When 'record=init', the LDA calculation on each atom is performed and an initial potential is generated. Then, configurations of core states are listed. The core configurations are set up in subroutine 'corcnf.f'. It is noticed that the core states must not come into the energy contour to avoid double counting of the core electrons.

After these output of initial conditions, the record of the self-consistent iteration is output. For each iteration loop, charge neutrality, spin moment, total energy and error (the average difference between input and output potentials) are shown to confirm a convergence. If the error becomes under a tolerance which is set in the subroutine 'specx.f', the iteration loop stops, and a result is printed out. If the number of loops exceeds 'maxitr', the iteration loop also stops. Lastly, from the obtained electronic structure, the hyperfine field, and so on, are calculated.

Table 2: Parameters used in 'specx.f'.

Parameter	Meaning
natmmx	maximum number of atoms in a unit cell.
ncnpmx	maximum number of types of atoms in a unit cell.
msizemx	maximum size of the KKR matrix. $\geq \sum_{i=1}^{natm}(l_{max,i}+1)^2$
mxlmx	$l \geq$mxlmx are truncated.
nk1mx,nk3mx	nk1mx+nk3mx is maximum number of k-points in the Brillouin zone.
msex	mesh points on the energy contour for go=dos, spc.
ngmx	The chebyshev expansion is performed up to ngmx-th order.
nrpmx	maximum number of lattice points used in the Ewalt's sum.
ngpmx	maximum number of reciprocal lattice points used in the Ewalt's sum.
msr	radial mesh points.
mse0	(data) mesh points on the energy contour for go=go.
tol	(data) tolerance of convergence

3.3 Parameters which define the size of arrays

By the way, size of an array used in the KKR program depends on a system to be calculated. It is necessary to reserve enough area. The size of the arrays in the KKR program is declared in the subroutine 'specx.f'. The parameters used in the 'specx.f' are summarized in table 2.

If unsuitable parameters are used in the input file or specx.f, the program will stop with an error message. Then, you can recognize what is wrong.

4 Exercises

1. Calculate the electronic structure of bcc Fe. Use the lattice constant $a = 5.27$ bohr and take magnetism into account. Does the obtained result show that Fe is ferromagnetic ? How large is the magnetic moment ?

2. Calculate the density of states of bcc Fe.

3. Estimate the lattice constant of Fe. First, calculate the electronic structure for various lattice constants. Then compare the total energy. The lattice constant which gives the lowest energy is realizable.

4. Calculate the electronic structure of fcc Ni. Use the lattice constant $a = 6.60$ bohr. Check the magnetic moment, density of states, lattice constant and so on.

5. **(Impurity problem)** Calculate bcc Fe with a single impurity which substitute a Fe atom. Plot the calculated hyperfine field as a function of the impurity's atomic number. Discuss the behavior of the hyperfine field.

6. **(Random alloy)** Calculate fcc Ni-Fe random alloy. Use the lattice constant of Ni. Discuss the density of states. What happens when the concentration of Fe is high ?

7. **(Random alloy)** Calculate various kinds of 3d transition metal alloys (Change combination of elements, concentration and structure). Plot the obtained magnetic moments as a function of the averaged atomic number. Thus obtained curve is called Slater-Pauling curve.

8. **(Local moment disorder)** Calculate the electronic structure of bcc Fe in the local moment disorder (LMD) state. We can treat the LMD state as a random alloy of Fe with up and down spin moments. Prepare the potential data file using /util/fmg.f

9. **(Local moment disorder)** In the mean-field theory, the Curie temperature $T_{\rm C}$ is evaluated as follows:

$$k_{\rm B}T_{\rm C} = \frac{2}{3}\left(E_{\rm LMD} - E_{\rm F}\right),$$

   where $k_{\rm B}$ is Boltsmann constant, $E_{\rm F}$ and $E_{\rm LMD}$ are total energy in the ferromagnetic and LMD states, respectively. Calculate Curie temperature from the obtained total energy. Use the values, $k_{\rm B} = 6.3336 \times 10^{-6}$Ry/K, if you need. Compare the results with the experimental value, $T_{\rm C}$(exp.) = 1043 K.

10. **(Local moment disorder)** Calculate the electronic structure of fcc Ni in the LMD state. Does the calculation works ? If not, discuss the reason.

11. Calculate the electronic structure of zinc-blende GaAs. The zinc-blende structure is constructed by the fcc structure. How is the input file ?

12. Put some defects in zinc-blende GaAs. Discuss the results.

13. Put some donors or accepters in zinc-blende GaAs. Discuss the results.

14. Put some magnetic impurities in zinc-blende GaAs. Discuss the results.

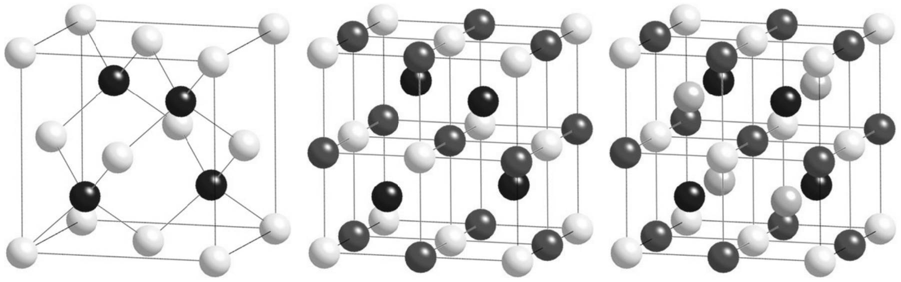

Figure 2: Zinc-blende, half-Heusler and full-Heusler structures.

More in Details

5 Density Functional Theory

5.1 Hohenberg-Kohn Theorem

The Hohenberg-Kohn theorem on which the density functional theory is established is explained according to the original paper.

An N-electron system under an external potential $v(r)$ is described with the following Hamiltonian H.

$$H = T + V + U, \tag{1}$$

where T is the kinematic energy, V is the potential energy and U is the Coulomb energy between electrons, i.e.,

$$\begin{aligned} T &= \sum_i -\nabla_i^2 && (2) \\ V &= \sum_i v(r_i) && (3) \\ U &= \sum_{i<j} \frac{2}{|r_i - r_j|}, && (4) \end{aligned}$$

where the atomic unit ($\hbar^2 = 1, e^2 = 2, m_e = 1/2$) is used. The N-electron wave function Φ satisfies the Schrödinger equation written as

$$H\Phi = E\Phi. \tag{5}$$

In the framework of the quantum theory, the ground state of the system, Ψ, under the given external potential v is obtained by the variational principle

$$\begin{aligned} H\Psi &= E_0\Psi && (6) \\ E_0[\Psi] &= \mathrm{Min}\langle\Psi|H|\Psi\rangle && (7) \\ \langle\Psi|\Psi\rangle &= N. && (8) \end{aligned}$$

Once the N-electron wave function Ψ is obtained, the density distribution ρ and any expectation values are obtained from Ψ. That is Ψ, ρ and expectation energy E_0 are the functionals of v.

$$\begin{aligned} \Psi &= \Psi[v] && (9) \\ \rho &= \rho[v] && (10) \\ E_0 &= E_0[v] && (11) \end{aligned}$$

In this procedure, we must deal with Ψ which has $3N$ degrees of freedom and must take the variation of the total energy functional with respect to Ψ.

If we can regard the density distribution ρ as a basic function in spite of Ψ, it will make the problem easier because ρ has only 3 degrees of freedom. It is shown that v is a functional of ρ by

Table 3: atomic unit

	unit
length	$\frac{\hbar^2}{m_e e^2} = 1(\mathrm{bohr}) = 0.529(\text{Å})$
energy	$\frac{m_e e^4}{2\hbar^2} = 1(\mathrm{Ry}) = 13.6(\mathrm{eV})$

the *reductio ad absurdum.* If the same ρ gives two different v and v', we get the different wave functions Ψ, Ψ' and the ground state energy E, E' according to the two different Hamiltonians H, H' associated with v, v' respectively. This leads the following two inequalities.

$$\begin{aligned} E' &= \langle \Psi' | H' | \Psi' \rangle \\ &< \langle \Psi | H' | \Psi \rangle \\ &= \langle \Psi | H - v + v' | \Psi \rangle \\ &= E + \int (v' - v) \rho dv \qquad (12) \\ E &= \langle \Psi | H | \Psi \rangle \\ &< \langle \Psi' | H | \Psi' \rangle \\ &= \langle \Psi' | H' - v' + v | \Psi' \rangle \\ &= E' + \int (v - v') \rho dv \qquad (13) \end{aligned}$$

The sum of these two inequalities gives the inconsistent result $E + E' < E' + E$. Therefore, v is a unique functional of ρ. In turn, the N-electron ground state wave function Ψ and all ground state properties are functionals of ρ.

$$\begin{aligned} v &= v[\rho] \qquad (14) \\ \Psi &= \Psi[\rho] \qquad (15) \\ \langle A \rangle &= \langle \Psi[\rho] | \hat{A} | \Psi[\rho] \rangle \\ &= A[\rho] \qquad (16) \end{aligned}$$

Next, the variational principle for $E_v[\rho]$ is derived. When Ψ and Ψ' are the ground states for given v and v' respectively, the following inequality is satisfied because of the variational principle of $E_v[\Psi]$ for Ψ.

$$E_v[\Psi] \leq E_v[\Psi'] \qquad (17)$$

Now, we introduce a new energy functional E_v defined as

$$\begin{aligned} E_v[\rho] &= \int \rho v dv + F[\rho] \qquad (18) \\ F[\rho] &= T[\rho] + U[\rho] \qquad (19) \end{aligned}$$

The variational principle for $E_v[\rho]$ for ρ is derived as

$$E_v[\rho] \leq E_v[\rho']. \qquad (20)$$

Because of the universality of the functional $F[\rho]$, once we know it, the ground state properties of any system can be determined.

5.2 Kohn-Sham Equations

Kohn and Sham developed an exact way to treat an inhomogeneous electron system from the theory of Hohenberg and Kohn. It has already shown that the total energy E_v of ground state for a given external potential v is written as,

$$\begin{aligned} E_v &= E_v[\rho] \\ &= \int v \rho dv + \frac{1}{2} \int \frac{\rho(r)\rho(r')}{|r - r'|} dr dr' + G[\rho], \qquad (21) \end{aligned}$$

where $G[\rho]$ was the universal functional of the density. G may be wrote as

$$G[\rho] = T_s[\rho] + E_{\mathrm{XC}}[\rho], \qquad (22)$$

where T_s is the kinetic energy of a non-interacting system of electrons. All of the many body effects are included into E_{XC}. To make a discussion clear, an effective potential V_{eff} is introduced, and E_v is divided into two terms such as

$$\begin{aligned} E_v[\rho] &= E_{\text{B}}[\rho] + E_{\text{D}}[\rho], & (23) \\ E_{\text{B}}[\rho] &= T_s + \int V_{\text{eff}}\rho dv, & (24) \\ E_{\text{D}}[\rho] &= -\int V_{\text{eff}}\rho dv + \int v\rho dv + E_{\text{H}} + E_{\text{XC}}. & (25) \end{aligned}$$

Therefore, the variational equation given by Hohenberg and Kohn, i.e.

$$\frac{\delta E_v}{\delta \rho} = 0, \tag{26}$$

is divided into a couple of the simultaneous equations:

$$\frac{\delta E_B}{\delta \rho} = 0, \quad \text{and} \quad \frac{\delta E_D}{\delta \rho} = 0. \tag{27}$$

Then the following variational equation called Kohn-Sham equations are derived.

$$\begin{aligned} -\nabla_i^2\psi_i(r) + V_{eff}(r)\psi_i(r) &= \epsilon_i\psi_i(r) & (28) \\ V_{eff}(r) &= v(r) + \int \frac{\rho(r')}{|r-r'|}dv' + V_{XC}(r) & (29) \\ \rho(r) &= \sum_i |\psi_i|^2 & (30) \\ V_{XC}(r) &= \frac{\delta \tilde{E}_{XC}[\rho]}{\delta \rho} & (31) \end{aligned}$$

5.3 Local density approximation

For a homogeneous electron gas, the exchange-correlation energy is accurately calculated.

$$\tilde{E}_{XC}[\rho]/N = \varepsilon_{XC}(\rho) \tag{32}$$

In the local density approximation (LDA), we regard an inhomogeneous electron system as a system locally homogeneous, i.e.,

$$\tilde{E}_{XC}[\rho] = \int \rho(r)\varepsilon_{XC}\left(\rho(r)\right)dv. \tag{33}$$

Therefore, the exchange-correlation potential is given by

$$V_{XC}(r) = \varepsilon_{XC}(\rho(r)) + \rho(r)\frac{d\varepsilon_{XC}(\rho(r))}{\rho(r)}. \tag{34}$$

5.4 Iteration

The self consistent Kohn-Sham equations are solved by an iteration procedure.

- Give a trial V_{eff}.
- Solve the single-electron Schrödinger equation.
- Calculate $\rho(r)$ by summing $\sum_i |\psi_i|^2$ up to the Fermi level.
- Solve the Poisson equation for $\rho(r)$ and construct the Hartree potential.
- Calculate V_{eff} using LDA.
- Compare the new and old V_{eff} and improve V_{eff}.

Repeat this procedure until the new and old potential become the same.

6 KKR-Green's function method

6.1 Single-Site problem

Let us consider the scattering due to a single potential at the origin. This potential vanishes at a region far from the origin.

6.1.1 Schrödinger equation

The Schrödinger equation which describes stationary states is

$$H\psi(\boldsymbol{r}) = [-\nabla^2 + V(\boldsymbol{r})]\psi = E\psi. \tag{35}$$

When the potential is spherical, the solutions are separable using the spherical coordinates:

$$\psi(\boldsymbol{r}) = R_l(r)Y_{lm}(\theta,\phi), \tag{36}$$

$$\left[-\frac{1}{r^2}\frac{d}{dr}r^2\frac{d}{dr} + \frac{l(l+1)}{r^2} + V(r) - E\right]R_l = 0, \tag{37}$$

$$\left[\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta} + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2} + \frac{l(l+1)}{r^2}\right]Y_{lm}(\theta,\phi) = 0. \tag{38}$$

The solution of the angular part is spherical harmonics. Using $R_l(r) = u_l(r)/r$, the radial equation is written as

$$\left[-\frac{d^2}{dr^2} + \frac{l(l+1)}{r^2} + V(r) - E\right]u_l(r) = 0. \tag{39}$$

The radial wave function is normalized as

$$\int_0^{R_{MT}} [rR_l(r;E)]^2 dr = 1. \tag{40}$$

6.1.2 Asymptotic form

The exact radial wave function outside the potential is

$$P_l(r;E) = A_l(E)j_l(\sqrt{E}r) + B_l(E)n_l(\sqrt{E}r). \tag{41}$$

j_l and n_l are the spherical Bessel and Neumann functions, which are regular and irregular at the origin, respectively. Outside the potential, whole wave function satisfying any particular bounding conditions has a form $\psi(\boldsymbol{r}) = \sum_L C_L(E)P_l(r;E)Y_L(\theta,\phi)$, where $L = (l,m)$. As the boundary condition, the wave function which represents scattering should have the following asymptotic form:

$$\psi(\boldsymbol{r}) \to e^{i\sqrt{E}z} + \frac{f(\theta)}{r}e^{i\sqrt{E}r}. \tag{42}$$

Therefore, $A_l(E)$and $B_l(E)$ can be expressed with a parameter $\eta_l(E)$ as

$$\begin{aligned} P_l(r;E) &= e^{i\eta_l}[\cos\eta_l j_l(\sqrt{E}r) + \sin\eta_l n_l(\sqrt{E}r)] \\ &\to e^{i\eta_l}\sin(\sqrt{E}r - \frac{l\pi}{2} + \eta_l). \end{aligned} \tag{43}$$

η_l is the phase shift of the wave function doe to the scattering of the single potential. Using the Hankel function of the first kind,

$$\begin{aligned} h_l^{(1)} &= j_l + in_l, & (44)\\ P_l(r;E) &= j_l(\sqrt{E}r) + ie^{\eta_l}\sin\eta_l h_l^{(1)}(\sqrt{E}r) \\ &= j_l(\sqrt{E}r) - i\sqrt{E}t_l(E)h_l^{(1)}(\sqrt{E}r). & (45)\end{aligned}$$

As a results, the scattering problem becomes the problem to obtain the t-matrix defined by

$$t_l(E) = -\frac{1}{\sqrt{E}}e^{i\eta_l}\sin\eta_l \tag{46}$$

6.1.3 Wronskian

Let us consider to construct the solution of the Schrödinger equation outside the potential range from the Wronskian relation. From the radial Schrödinger equations,

$$\begin{aligned} \left[-\frac{d^2}{dr^2} + \frac{l(l+1)}{r^2} + V(r) - E\right] rP_l(r;E) &= 0, & (47)\\ \left[-\frac{d^2}{dr^2} + \frac{l(l+1)}{r^2} - E\right] r\begin{pmatrix} j_l(\sqrt{E}r) \\ n_l(\sqrt{E}r)\end{pmatrix} &= 0, & (48)\end{aligned}$$

the following integrals are evaluated.

$$\begin{aligned} \int_0^r rj_l(\sqrt{E}r)V(r)rP_l(r;E)dr &= W[rj_l(\sqrt{E}r), rP_l(r,E)]_r, & (49)\\ \int_r^\infty rn_l(\sqrt{E}r)V(r)rP_l(r;E)dr &= -\frac{1}{\sqrt{E}}e^{i\eta_l}\cos\eta_l - W[rn_l(\sqrt{E}r), rP_l(r,E)]_r. & (50)\end{aligned}$$

The first term in Eq. (50) is obtained from the asymptotic form of $P_l(r;E)$. Wronskian is defined as

$$W[a(r), b(r)] = a(r)\frac{db(r)}{dr} - \frac{da(r)}{dr}b(r). \tag{51}$$

Multipling Eq. (49) by $n_l(\sqrt{E})$ and $j_l(\sqrt{E})$ to Eq. (50) by $n_l(\sqrt{E})$, and summing these equations, we obtain

$$\begin{aligned} P_l(r;E) &= e^{i\eta_l}\cos\eta_l j_l(\sqrt{E}r) - \sqrt{E}\int_0^\infty j_l(\sqrt{E}r_<)n_l(\sqrt{E}r_>)V(r')P_l(r';E)r'^2dr' \\ &\to e^{i\eta_l}\cos\eta_l j_l(\sqrt{E}r) - \sqrt{E}n_l(\sqrt{E}r)\int_0^\infty j_l(\sqrt{E}r')V(r')P_l(r';E)r'^2dr' \\ &= e^{i\eta_l}[\cos\eta_l j_l(\sqrt{E}r) - \sin\eta_l n_l(\sqrt{E}r)] \\ &= C_l(E)j_l(\sqrt{E}r) - S_l(E)n_l(\sqrt{E}r) \\ &= [C_l(E) - iS_l(E)]\, j_l(\sqrt{E}r) + iS_l(E)h_l^{(1)}(\sqrt{E}r), & (52)\end{aligned}$$

where

$$\begin{aligned} C_l(E) &= e^{i\eta_l}\cos\eta_l \\ &= \sqrt{E}W[rP_l(r;E), rn_l(\sqrt{E}r)]_{r>R_{MT}}, & (53)\\ S_l(E) &= e^{i\eta_l}\sin\eta_l \\ &= -\sqrt{E}W[rP_l(r;E), rj_l(\sqrt{E}r)]_{r>R_{MT}}. & (54)\end{aligned}$$

As a results, t-matrix is calculated from Wronskian:

$$t_l(E) = -\frac{1}{\sqrt{E}}\frac{S_l(E)}{C_l(E) - iS_l(E)}. \tag{55}$$

6.1.4 Green's function in the free space

Green's function in the free space is defined as

$$[\nabla^2 + E]g(\boldsymbol{r}, \boldsymbol{r'}) = \delta(\boldsymbol{r} - \boldsymbol{r'}). \tag{56}$$

The solution is obtained using the Fourier transformation

$$\begin{aligned} g(\boldsymbol{r}, \boldsymbol{r'}) &= g(\boldsymbol{r} - \boldsymbol{r'}) \\ &= -\frac{e^{(i\sqrt{E}|\boldsymbol{r}-\boldsymbol{r'}|)}}{4\pi|\boldsymbol{r} - \boldsymbol{r'}|}. \end{aligned} \tag{57}$$

In addition, it is expanded into the partial waves as

$$g(\boldsymbol{r}, \boldsymbol{r'}) = -i\sqrt{E}\sum_L j_l(\sqrt{E}r_<)Y_L(\boldsymbol{r_<})h_l^{(1)}(\sqrt{E}r_>)Y_L(\boldsymbol{r_>}). \tag{58}$$

Consider an inhomogeneous differential equation,

$$[\nabla^2 + E]\phi_L(\boldsymbol{r}) = V(r)\phi_L(\boldsymbol{r}). \tag{59}$$

Its general solution is expressed as a sum of its particular solution and the general solution to the homogeneous differential equation,

$$[\nabla^2 + E]\phi_L^0(\boldsymbol{r}) = 0. \tag{60}$$

Since a particular solution can be obtained from Green's function, the general solution is

$$\phi_L(\boldsymbol{r}) = Z_L(E)\phi_L^0(\boldsymbol{r}) + \int g(\boldsymbol{r} - \boldsymbol{r'})V(r')\phi_L(\boldsymbol{r'})d\boldsymbol{r'}, \tag{61}$$

where $Z_L(E)$ is a normalization constant.

6.2 Traditional KKR

6.2.1 Muffin-tin potential

Usually, the KKR method is formulated using the muffin-tin potential approximation. Under this approximation, the Schrödinger equation can be solved exactly.

The potentials are approximated as

$$v(\boldsymbol{r}) = \begin{pmatrix} v(r) \text{ for } r < R_{MT} \\ 0 \text{ for } r > R_{MT}, \end{pmatrix} \tag{62}$$

where the origin is taken at the center of the atomic sphere. R_{MT} is the radius of the sphere which does not overlapped each other.

In the muffin-tin approximation, a constant potential is assumed in the interstitial region. The origin of the energy is chosen such that potential at the interstitial region is zero as shown in Fig. 3.

6.2.2 Cell-centered expantion

Let us consider the Schrödinger equation,

$$[-\nabla^2 + V(r)]\psi(\boldsymbol{r}) = E\psi(\boldsymbol{r}). \tag{63}$$

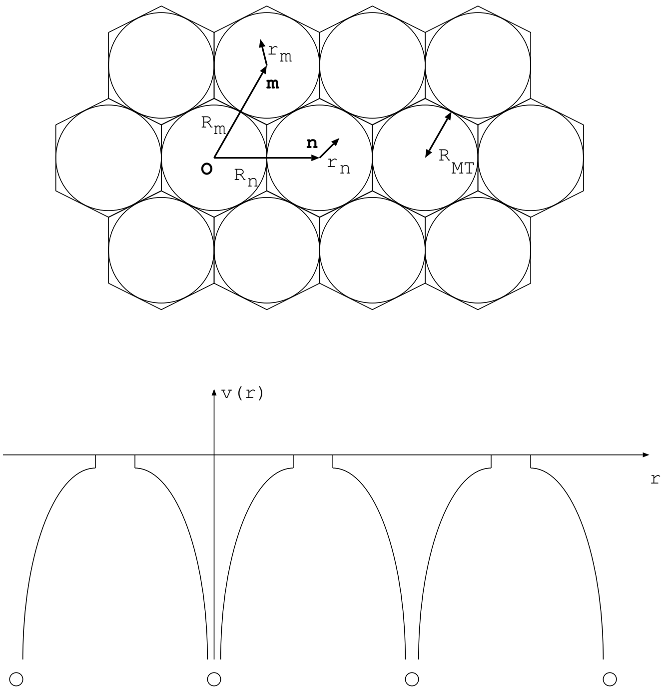

Figure 3: Muffin-tin potential

Using the free space Green's function, $\psi(\boldsymbol{r})$ can be written as

$$\begin{aligned}\psi(\boldsymbol{r}) &= \int g(\boldsymbol{r},\boldsymbol{r'})V(\boldsymbol{r'})\psi(\boldsymbol{r'})dv' \\ &= \int g(\boldsymbol{R_m}+\boldsymbol{r_m},\boldsymbol{R_n}+\boldsymbol{r'_n})\sum_n v(\boldsymbol{R_n}+\boldsymbol{r'_n})\psi(\boldsymbol{R_n}+\boldsymbol{r'_n})dv'_n \\ &= \sum_n \int g(\boldsymbol{r_m},\boldsymbol{R_n}-\boldsymbol{R_m}+\boldsymbol{r'_n})v(\boldsymbol{r'_n})\psi(\boldsymbol{r'_n})dv'_n. \qquad (64)\end{aligned}$$

Here, $\psi(r)$ is expanded into the atomic wave functions in the m-th sphere ψ^m_L as

$$\psi(\boldsymbol{r}) = \sum_L C^m_L \phi^m_L(\boldsymbol{r_m}). \qquad (65)$$

ϕ^m_L satisfies the Shcrödinger equation in the m-th sphere and expressed by using g,

$$\begin{aligned}[-\nabla^2 + v(\boldsymbol{r})]\phi^m_L(\boldsymbol{r}) &= E\phi^m_L(\boldsymbol{r}), \qquad (66)\\ \phi^m_L(\boldsymbol{r}) &= Z^m_L(E)\phi^0_L(\boldsymbol{r}) + \int g(\boldsymbol{r},\boldsymbol{r'})v(\boldsymbol{r'})\phi^m_L(\boldsymbol{r'})dv'. \qquad (67)\end{aligned}$$

Substituting these expressions, we obtain

$$\begin{aligned}&\sum_L C^m_L[Z^m_L(E)\phi^0_L(\boldsymbol{r_m}) + \int g(\boldsymbol{r_m},\boldsymbol{r'_m})v(\boldsymbol{r'_m})\phi^m_L(\boldsymbol{r'_m})dv'_m] \\ = &\sum_n \int g(\boldsymbol{r_m},\boldsymbol{R_n}-\boldsymbol{R_m}+\boldsymbol{r'_n})v(\boldsymbol{r'_n})\sum_L C^n_L\phi^n_L(\boldsymbol{r'_n})dv'_n. \qquad (68)\end{aligned}$$

6.2.3 Structure constant

$g(\boldsymbol{r_m},\boldsymbol{R_n}-\boldsymbol{R_m}+\boldsymbol{r'_n})$ is expanded into the partial waves as

$$g(\boldsymbol{r_m},\boldsymbol{R_n}-\boldsymbol{R_m}+\boldsymbol{r'_n}) = -i\sqrt{E}\sum_L j_l(\sqrt{E}r_m)Y_L(\boldsymbol{r_m})$$

$$
\begin{aligned}
& \times h_l^{(1)}(\sqrt{E}|\boldsymbol{r'_n}+\boldsymbol{R_n}-\boldsymbol{R_m}|)Y_L(\boldsymbol{r'_n}+\boldsymbol{R_n}-\boldsymbol{R_m}) \\
= \; & -i\sqrt{E}\sum_L j_l(\sqrt{E}r_m)Y_L(\boldsymbol{r_m}) \\
& \times 4\pi \sum_{L',L''} i^{l-l'+l''}C_{LL'L''}h_{l''}^{(1)}(\sqrt{E}|\boldsymbol{R_n}-\boldsymbol{R_m}|) \\
& \times Y_{L''}(\boldsymbol{R_n}-\boldsymbol{R_m})j_{l'}(\sqrt{E}r'_n)Y_{L'}(\boldsymbol{r'_n}) \\
= \; & \sum_{LL'}\phi_L^0(\boldsymbol{r_m})g_{LL'}^{mn}\phi_{L'}^0(\boldsymbol{r'_n}),
\end{aligned}
\tag{69}
$$

$$
g_{LL'}^{mn} = -i4\pi\sqrt{E}\sum_{L''}i^{l-l'+l''}C_{LL'L''}h_{l''}^{(1)}(\sqrt{E}|\boldsymbol{R_n}-\boldsymbol{R_m}|)Y_{L''}(\boldsymbol{R_n}-\boldsymbol{R_m}). \tag{70}
$$

$g_{LL'}^{mn}$ is called the structure constant. It depends only on the lattice structure, not on the potential at the lattice point.

6.2.4 KKR-matrix

From the partial wave expansion of Green's function, we can obtain the equation that the expansion coefficients of the wave function should satisfy:

$$
\begin{aligned}
\sum_L C_L^m[Z_L^m(E)\phi_L^0(\boldsymbol{r_m}) \; + \; & \int g(\boldsymbol{r_m},\boldsymbol{r'_m})v(\boldsymbol{r'_m})\phi_L^m(\boldsymbol{r'_m})dv'_m] \\
= \; & \sum_{n\neq m}\int\sum_{LL'}\phi_L^0(\boldsymbol{r_m})g_{LL'}^{mn}\phi_{L'}^0(\boldsymbol{r'_n})v(\boldsymbol{r'_n})\sum_L C_L^n\phi_L^n(\boldsymbol{r'_n})dv'_n \\
& +\int g(\boldsymbol{r_m},\boldsymbol{r'_m})v(\boldsymbol{r'_m})\phi_L^m(\boldsymbol{r'_m})dv'_m,
\end{aligned}
\tag{71}
$$

$$
\begin{aligned}
\sum_L C_L^m Z_L^m(E)\phi_L^0(\boldsymbol{r_m}) \; = \; & \sum_L\phi_L^0(\boldsymbol{r_m})\sum_{n\neq m}\sum_{L'}g_{LL'}^{mn}\int\phi_{L'}^0(\boldsymbol{r'_n})v(\boldsymbol{r'_n})\phi_L^n(\boldsymbol{r'_n})dv'_nC_{L'}^n \\
= \; & \sum_L\phi_L^0(\boldsymbol{r_m})\sum_{n\neq m}\sum_{L'}g_{LL'}^{mn}Y_{L'}^n(E)C_{L'}^n.
\end{aligned}
\tag{72}
$$

This leads to the secular equation

$$
\sum_{L'n}\left[\delta_{LL'}\delta_{mn}Z_L^m(E)-g_{LL'}^{mn}Y_{L'}^n(E)\right]C_{L'}^n = 0. \tag{73}
$$

Here, $Z_L^m(E)$ and $Y_{L'}^m(E)$ are

$$
\begin{aligned}
Z_L^m(E) &= C_l^m(E)-iS_l^m(E), \qquad (74) \\
Y_{L'}^m(E) &= S_l^m(E). \qquad (75)
\end{aligned}
$$

Therefore,

$$
\det\left[\delta_{LL'}\delta_{mn}-g_{LL'}^{mn}t_{L'}^n(E)\right] = 0 \tag{76}
$$

must be satisfied.

6.3 Crystal Green's Function

6.3.1 Integral equation

In the previous section, we constructed the wave functions of scattered electrons using the free space Green's function. In this section, the Green's function of the system $G(\boldsymbol{r},\boldsymbol{r'})$ is constructed.

$$
[\nabla^2+E-V(r)]G(\boldsymbol{r},\boldsymbol{r'}) = \delta(\boldsymbol{r}-\boldsymbol{r'}) \tag{77}
$$

Transposing the potential term to r.h.s. as

$$\begin{aligned}[\nabla^2 + E]G(\boldsymbol{r},\boldsymbol{r'}) &= V(r)G(\boldsymbol{r},\boldsymbol{r'}) + \delta(\boldsymbol{r}-\boldsymbol{r'}) \\ &= f(\boldsymbol{r},\boldsymbol{r'}),\end{aligned} \tag{78}$$

we find that G is expressed as

$$\begin{aligned}G(\boldsymbol{r},\boldsymbol{r'}) &= \int g(\boldsymbol{r},\boldsymbol{r''})f(\boldsymbol{r''},\boldsymbol{r'})dv'' \\ &= g(\boldsymbol{r},\boldsymbol{r'}) + \int g(\boldsymbol{r},\boldsymbol{r''})V(r'')G(\boldsymbol{r''},\boldsymbol{r'})dv''.\end{aligned} \tag{79}$$

6.3.2 Dyson equation

The free space Green's function is expanded as

$$g(\boldsymbol{r}+\boldsymbol{R_m},\boldsymbol{r'}+\boldsymbol{R_n}) = \delta_{mn}g(\boldsymbol{r},\boldsymbol{r'}) + \sum_{LL'} J_L(\boldsymbol{r})g^{mn}_{LL'}J_{L'}(\boldsymbol{r'}), \tag{80}$$

$$g(\boldsymbol{r},\boldsymbol{r'}) = -i\sqrt{E}\sum_{L} J_L(\boldsymbol{r_<})H_L(\boldsymbol{r_>}). \tag{81}$$

where

$$J_L(\boldsymbol{r}) = j_l(\sqrt{E}r)Y_L(\boldsymbol{r}), \tag{82}$$

$$H_L(\boldsymbol{r}) = h^{(1)}_l(\sqrt{E}r)Y_L(\boldsymbol{r}). \tag{83}$$

Similarly $G(r,r')$ is expressed as

$$G(\boldsymbol{r}+\boldsymbol{R_m},\boldsymbol{r'}+\boldsymbol{R_n}) = \delta_{mn}G^m_s(\boldsymbol{r},\boldsymbol{r'}) + \sum_{LL'} \mathcal{J}_L(\boldsymbol{r})G^{mn}_{LL'}\mathcal{J}_{L'}(\boldsymbol{r'}), \tag{84}$$

$$G^m_s(\boldsymbol{r},\boldsymbol{r'}) = -i\sqrt{E}\sum_{L} \mathcal{J}_L(\boldsymbol{r_<})\mathcal{H}_L(\boldsymbol{r_>}), \tag{85}$$

$$\mathcal{J}_L(\boldsymbol{r}) = P_l(\sqrt{E}r)Y_L(\boldsymbol{r}), \tag{86}$$

$$\mathcal{H}_L(\boldsymbol{r}) = Q_l(\sqrt{E}r)Y_L(\boldsymbol{r}). \tag{87}$$

The direct insertion of this formula to the integral equation yields the expansion coefficients G^{mn}_{LL}

$$G^{mn}_{LL'} = g^{mn}_{LL'} + \sum_{L''l} g^{ml}_{LL''}t^l_{L''}G^{ln}_{L''L'}. \tag{88}$$

6.3.3 Periodic boundary condition

When the scattering centers are aligned periodically such as in a crystal, $G^{mn}_{LL'}$ and $g^{mn}_{LL'}$ are Fourier transformed as

$$G^{mn}_{LL'} = \frac{1}{\tau}\int_{1stBZ} G_{LL'}(\boldsymbol{k})e^{-i\boldsymbol{k}(\boldsymbol{R_m}-\boldsymbol{R_n})}d\boldsymbol{k}, \tag{89}$$

$$g^{mn}_{LL'} = \frac{1}{\tau}\int_{1stBZ} g_{LL'}(\boldsymbol{k})e^{-i\boldsymbol{k}(\boldsymbol{R_m}-\boldsymbol{R_n})}d\boldsymbol{k}. \tag{90}$$

Substituting them into Eq. (88) yields

$$G_{LL'}(\boldsymbol{k}) = g_{LL'}(\boldsymbol{k}) + \sum_{L''} g_{LL''}(\boldsymbol{k})t_{L''}G_{L''L'}(\boldsymbol{k}). \tag{91}$$

We finally obtain the equation,

$$G_{LL'}(\boldsymbol{k}) = \sum_{L''}\left[\delta_{L''L} - g_{L''L}(\boldsymbol{k})t_L\right]g_{L''L'}(\boldsymbol{k}). \tag{92}$$

6.3.4 Density of States

The electron density distribution is directly obtained from the Green's function of the system. It is shown from the eigen function expansion of the Green's function.

The eigenfunction ϕ_n of the Schrödinger equation $H\phi = E\phi$ which associated with the eigenvalue E_n and the Green's function of the system satisfy

$$\mathcal{H}\phi_n = E_n\phi_n, \tag{93}$$

$$[E - \mathcal{H}]G(\boldsymbol{r}, \boldsymbol{r'}) = \delta(\boldsymbol{r} - \boldsymbol{r'}). \tag{94}$$

Expanding $G(r, r')$ into ϕ_n's with the expansion coefficients $G_n(r')$,

$$G(\boldsymbol{r}, \boldsymbol{r'}) = \sum_n G_n(\boldsymbol{r'})\phi_n(\boldsymbol{r}), \tag{95}$$

and multiplying it by $(E - H)$ from the left, we obtain

$$\begin{aligned} (E - \mathcal{H})G(\boldsymbol{r}, \boldsymbol{r'}) &= \sum_n G_n(\boldsymbol{r'})(E - \mathcal{H})\phi_n(\boldsymbol{r}), \\ &= \delta(\boldsymbol{r} - \boldsymbol{r'}). \end{aligned} \tag{96}$$

Multiplying Eq. (96) by $\phi_m^*(r)$ and the volume integration leads to

$$G_n(\boldsymbol{r'}) = \phi^*(\boldsymbol{r'})/(E - E_n). \tag{97}$$

Therefore,

$$G(\boldsymbol{r}, \boldsymbol{r'}) = \sum_n \frac{\phi_n^*(\boldsymbol{r'})\phi_n(\boldsymbol{r})}{E - E_n} \tag{98}$$

is obtained. With an identity

$$\frac{1}{x + i\epsilon} = \mathrm{P.}\frac{1}{x} - i\pi\delta(x), \tag{99}$$

$$\begin{aligned} G(\boldsymbol{r}, \boldsymbol{r'}) &= \sum_n \frac{\phi_n^*(\boldsymbol{r'})\phi_n(\boldsymbol{r})}{E + i\epsilon - E_n} \\ &= \mathrm{P.}\sum_n \frac{\phi_n^*(\boldsymbol{r'})\phi_n(\boldsymbol{r})}{E - E_n} - i\pi \sum_n \delta(E - E_n)\phi_n^*(\boldsymbol{r'})\phi_n(\boldsymbol{r}) \end{aligned} \tag{100}$$

is obtained. This gives the expression for the electron density distribution ρ

$$\begin{aligned} \rho(\boldsymbol{r}, E) &= \sum_n \delta(E - E_n)\phi_n^*(\boldsymbol{r})\phi_n(\boldsymbol{r}) \\ &= -\frac{1}{\pi}\mathrm{Im}G(\boldsymbol{r}, \boldsymbol{r}). \end{aligned} \tag{101}$$

Therefore, once the Green's function of the crystal is known, we obtain the electron density directly from it.

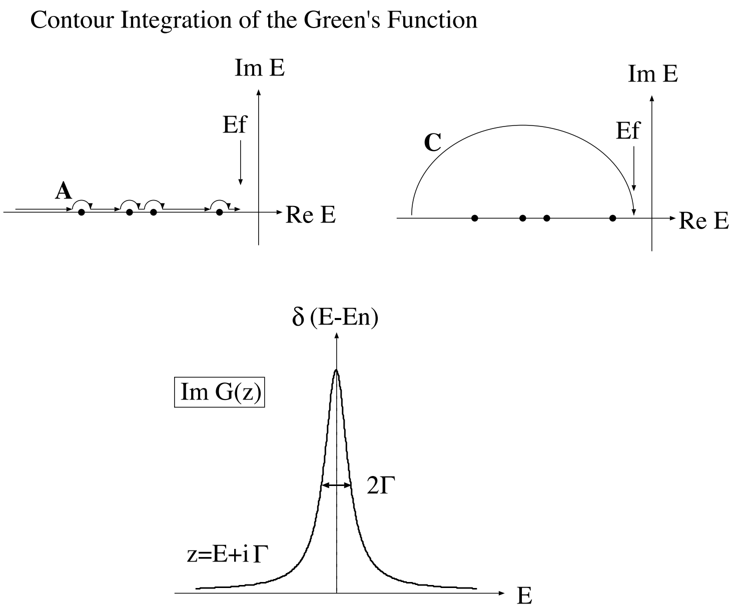

Figure 4: Contour integration of the Green's Function

6.3.5 Contour integration

Now, the density distribution is calculated from the crystal Green's function. To obtain the density distribution of electrons, it is needed to integrate the Green's function with respect to the energy accurately. However, it is rather difficult because of the many-peaked structure of the density of states. To overcome this difficulty the contour integration technique is often employed. First, the Green's function is continuated to the complex energy plane.

$$
\begin{aligned}
G(\boldsymbol{r},\boldsymbol{r};z) &= \sum_n \frac{\phi_n^*(\boldsymbol{r})\phi_n(\boldsymbol{r})}{z-E} \\
&= \int_{-\infty}^{\infty} \sum_n \delta(E'-E_n)\frac{\phi_n^*(\boldsymbol{r})\phi_n(\boldsymbol{r})}{z-E'}dE' \\
&= -\frac{1}{\pi}\int_{-\infty}^{\infty} \mathrm{Im}G(\boldsymbol{r},\boldsymbol{r'};E')/(z-E')dE' \qquad (102)
\end{aligned}
$$

Here, G(z) is analytic in the whole complex plane except on the real axis. So we can deform the integration path arbitrary in the complex plane.

$$
\begin{aligned}
n(\boldsymbol{r}) &= \sum_n |\phi_n(\boldsymbol{r})|^2 \\
&= \int_{-\infty}^{E_F} \rho(\boldsymbol{r},E)dE \\
&= -\frac{1}{\pi}\int_{-\infty}^{E_F} \mathrm{Im}G(\boldsymbol{r},\boldsymbol{r};E)dE \\
&= -\frac{1}{\pi}\int_{A} \mathrm{Im}G(\boldsymbol{r},\boldsymbol{r};z)dz \\
&= -\frac{1}{\pi}\int_{C} \mathrm{Im}G(\boldsymbol{r},\boldsymbol{r};z)dz \qquad (103)
\end{aligned}
$$

The contour integration can be performed accurately, because the peaked structure of the DOS is smeared out. At $z = E + i\Gamma$, G(z) is

$$
\mathrm{Im}G(\boldsymbol{r},\boldsymbol{r};z) = \mathrm{Im}G(\boldsymbol{r},\boldsymbol{r};E+i\Gamma)
$$

$$= \frac{1}{\pi}\int_{-\infty}^{\infty} \mathrm{Im}G(E')\frac{\Gamma}{(E'-E)^2-\Gamma^2}dE'. \tag{104}$$

This means the delta function on the real axis is broadened into the Lorentzian shape with the half-width of Γ (Fig. 4).

6.4 Coherent potential approximation (CPA)

Let us consider a random alloy system which consists of n components, A_1, A_2, ... A_n and their concentrations are $x_1, x_2, ...x_n$. Suppose that the atom A_i is at the origin in the effective medium. Green's function which starts from the origin and comes back to the origin is

$$G^i_{LL'} = \sum_{L''} \tilde{G}_{LL''}\left[1-(t_i-\tilde{t})\tilde{G}\right]^{-1}_{L''L'}. \tag{105}$$

$\tilde{G}_{LL'}$ and $\tilde{t}$ are the Green's function and t-matrix (coherent t-matrix) of the effective medium, respectively. CPA is an efficient approximation to determine $\tilde{t}$. We use the self-consistent equation,

$$\sum_{i=1}^{n} x_i G^i_{LL'} = \tilde{G}_{LL'}. \tag{106}$$

This equation means that we determine the Green's function of the medium by taking weighted average of the Green's function where the component atom is placed at the origin in the effective medium (see Fig. (5)).

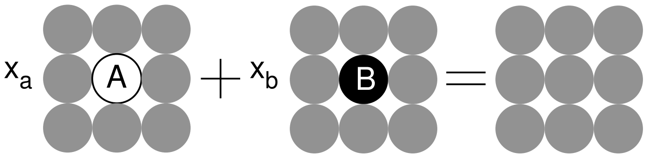

Figure 5: Idea of CPA.

7 Subroutines

The KKR package consists of over 100 subroutines. Here, to get a survey of the KKR package, a brief flowchart is given in Fig. 6. A comment on each subroutine is also given in table 4.

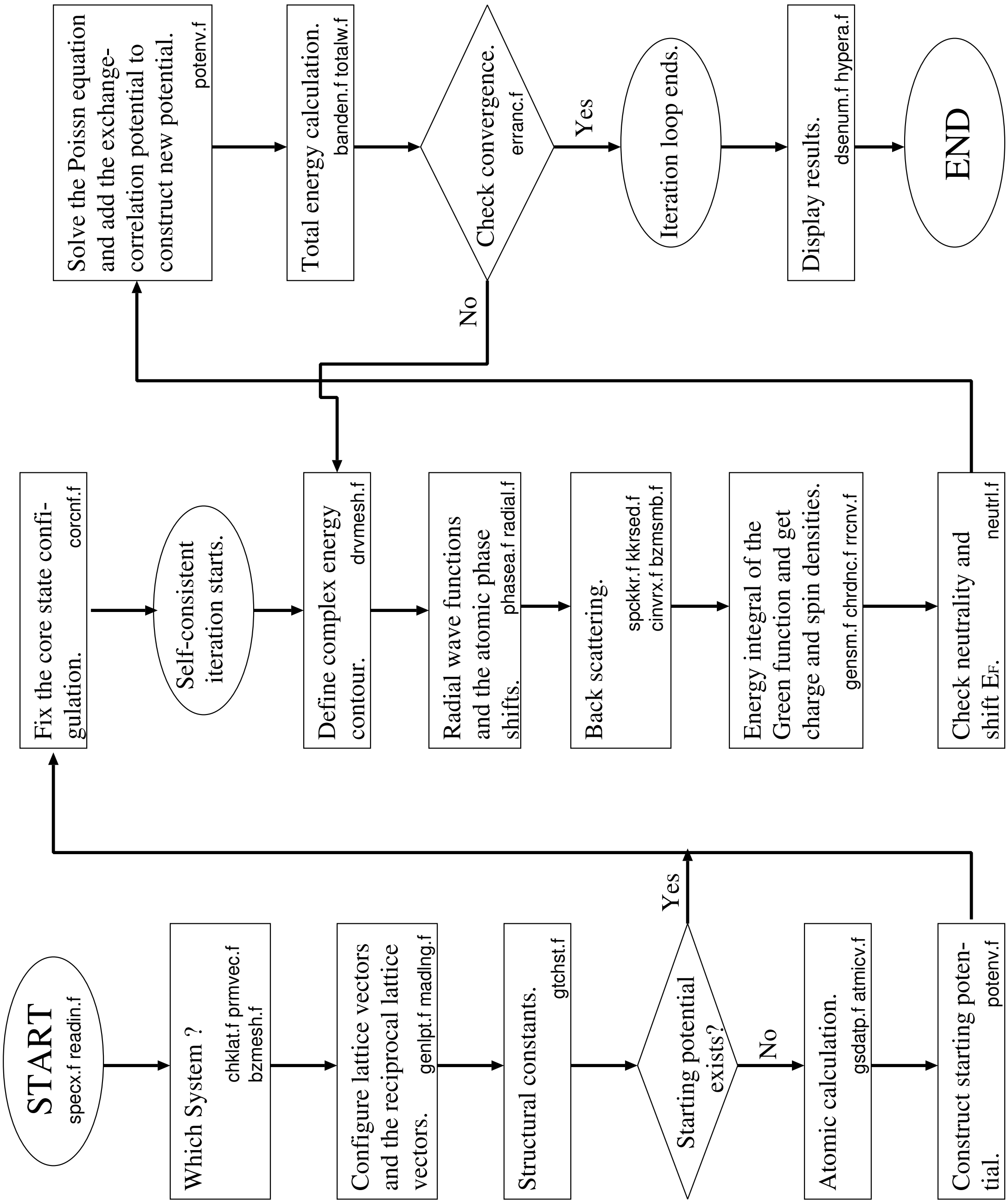

Figure 6: The flow chart of the band structure calculation.

Table 4: Subroutines in the KKR package.

Subroutine	Comment
specx.f	Some parameters and arrays are defined and spmain is called.
readin.f	A given input file is read in.
spmain.f	Main routine of the KKR.
chklat.f	Check muffin tin radii and modify them if they conflict.
prmvec.f	The primitive lattice vector and the reciprocal lattice vector are generated.
bzmesh.f	k-points in the Brillouin zone are set up.
genlpt.f	Lattice points in the real and reciprocal space are generated.
madlng.f	The madelung constants are calculated.
gtchst.f	The KKR structure constants are calculated.
gsdatp.f	Initial potentials are constructed from the atomic calculations.
atmicv.f	The atomic calculation is performed.
corcnf.f	The configuration of the core states is confirmed.
drvmsh.f	The energy contour is defined.
phasea.f	The atomic t-matrix is calculated.
radial.f	The radial Schrödinger equation is solved.
fczero.f	Single site Green's function.
cstate.f	The radial Schrödinger equation is solved for the core states.
spckkr.f	The crystal Green's function is constructed.
kkrsed.f	The structure constant are interpolated for each energy point.
cinvrx.f	$(1-gt)^{-1}$ is calculated.
bzmsmb.f	Integration in k-space.
chrdnc.f	The charge density distribution is calculated.
neutrl.f	The charge neutrality is calculated and ϵ_f is shifted.
potenv.f	The Poisson equation is solved. The exchange-correlation potential is calculated.
banden.f	The energy eigenvalues are summed up.
totalw.f	The total energy of the system is calculated.
erranc.f	The convergence is checked, and new input potential is constructed.
dsenum.f	The results are printed out.
hypera.f	The hyperfine field is calculated.

8 References

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