The Multichannel Multiple Scattering (MCMS) Program

[Peter Krüger, 2016]

- currently only for $L_{2,3}$-edge XAS with particle–hole wave function

- magnetic systems possible but not shown here

Calculated spectra [`spectrum.dat`]:

- isotropic spectrum $I_{\text{iso}}(\omega) = \sum_q I_q(\omega)$

- polarization: linear x, y, z, circular left/right $(+/-)$ for $\mathbf{k} \sim z$

- arbitrary polarisation can be found from $I_{qq'}(\omega)$ [`specqqprime.dat`]
e.g. circular dichroism for $\mathbf{k} \sim z$, $I_{CD} = I_{++} - I_{--}$

- spectral decomposition in final state d-orbitals $I_{mm'}(\omega)$ [`specmmprime.dat`]

Some features of the code

- most parts written in ANSI C − dynamical memory allocation.

- calls LAPACK library routines (in Fortran 77)

- calls CONTINUUM [C. R. Natoli] for $G^{ij}_{LL'}$
  − written in Fortran 77 with static memory allocation

Program Flow

- `readinput`   (FILE mcms.in)

- `readlmtopot`   (absorber potential FILEs)

- `readcofi`   (core wave function FILE)

- construct partially screened potential

- if the FILE `rhochi.dat` exists, read it

  (`rhochi.dat` contains reflectivity)

- otherwise call `environment` which calculates reflectivity on (fine) energy mesh $\{\ \epsilon_i\ \}$ through standard M.S. calculation

– read `instr.dat` = structure file

– `readlmtopot`   (all potential FILEs)

   For all photoelectron energies ϵ_i:

– calculate t-matrices and radial matrix elements of all atoms

– call `CONTINUUM` which calculates $G^{ij}_{LL'}$ and sets up MS matrix.

– invert MS matrix

– return reflectivity(ϵ_i) to `main`

• calculate basis orbitals (open + closed) for R-matrix

• make electronic configurations and N-electron basis states = Slater-determinants − no angular momentum coupling

- calculate matrix elements of hamiltonian between Slater determinants
  − most complicated are those of Coulomb operator

- calculate (N-electron) matrix elements of dipole operator

- calculate (N-electron) matrix elements of Q and L

  Begin total (or photon) energy E loop

- Solve eigen-channel eqs (=generalized eigenvalue problem)
$$\sum_{\nu}(E - H - L)_{\mu\nu}c_{\nu k} = \sum_{\nu} Q_{\mu\nu}c_{\nu k}b_{k}$$

- $\rightarrow$ R-matrix

- match with Bessel, Neumann-functions
  $\rightarrow \mathcal{T}^{-1} =$ inverse of multichannel T-matrix (E)

- $M = \mathcal{T}^{-1} - \rho \quad \rightarrow$ pick up $\rho(\epsilon_\alpha)$ by interpolating $\rho(\epsilon)$

- invert $M \quad \Rightarrow \quad \tau^{00}_{\alpha\beta}$

- calculate dipole matrix elements $M_{\alpha L} = \langle \Psi_{\alpha L} | r_q | \Psi_g \rangle$

- calculate XAS cross section $\quad I_q(E) = -\sum_{\alpha\beta} M^*_\alpha \, \mathrm{Im}\tau^{00}_{\alpha\beta} \, M_\beta$

  End total (or photon) energy E loop

Input files

- 1 structure file: `instr.dat`

- 1 potential file for each inequivalent atom in the system:
e.g. CaO: at least `Ca, O`
better 1 extra file for final-state rule potential (fully relaxed) `Ca_ch`

- core-orbital file

- main input file   `mcms.in`
contains parameters of calculation

The structure file   `instr.dat`

```
   27    27     2
 Ca_01  3  20     0.000000      0.000000      0.000000
  O_02  1   8     0.000000     -4.544792      0.000000
 Ca_03  2  20     0.000000      4.544792      4.544792
  O_04  1   8    -4.544792      4.544792      4.544792
  O_02  1   8    -4.544792      0.000000      0.000000
  O_02  1   8     0.000000      0.000000      4.544792
  O_02  1   8     4.544792      0.000000      0.000000
  O_02  1   8     0.000000      0.000000     -4.544792
  O_02  1   8     0.000000      4.544792      0.000000
 Ca_03  2  20     4.544792      0.000000     -4.544792
  ...
  O_04  1   8     4.544792     -4.544792     -4.544792
  ...
```

1st line: `number of atoms, number of atoms, 2`

all other lines (as many as atoms):

` potfilename     lmax     Z     x     y     z`

(x,y,z in Bohr radii $= 0.529177$ Angs)

The potential files `any_name`

EITHER:

use LMTO potential files

```
GENERAL: LMX=2  NSPIN=1   WSR= 2.300000  REL=F  NR=309  A=.030
   Z=22  QC=18  QTOT=-1.657339
...
POT:
  309     1      0.03000      2.30000
 1.446896229E+02 1.446896215E+02 1.446896172E+02 1.446896098E+02 1.446899148E+02
 ...
 ...
 1.948503960E+01 1.893767293E+01 1.839966378E+01 1.787094852E+01
...
```

OR:

generate "LMTO-formatted" files from `POTGEN/PHAGEN` potential files using utility program `readhspot`.

– Take a potential file (in potgen format): e.g. xalpha.pot

– Run the programs

```
transformhspot < xalpha.pot > C_readable.pot
```

```
readhspot C_readable.pot
```

This generates the input file `instr.dat` and one potential-file for each inequivalent atom in LMTO format. These files are named `X_01 Y_02` etc where X,Y are the symbols of the elements.

```
LMTO-type pot-file generated from H.S. pot-file
Z= 20
POT:
  321     1      0.03000      2.99000
 0.000000000e+00 9.726327137e+01 9.726687378e+01 9.727058367e+01 9.727440416e+01
  ...
 1.420510254e+01 1.377548513e+01 1.335201620e+01 1.293418401e+01 1.252140073e+01
 1.211308769e+01
```

The main input file   `mcms.in`

- format:

`KEYWORD VALUE [any comment] KEYWORD VALUE ...`

- order irrelevant

- some variables have default values (. . . danger . . .)

- comments at any place **except** between a `KEYWORD` and its `VALUE`

- energy unit: **Rydberg** on input, **eV** on output (spectra)

- `KEYWORD`'s are **case sensitive**

Example of `mcms.in`

```
AbsCHPotFile        Ca_ch         % final state potential file
CoreWFFile          ca_2p_ch      % core wave function file
PhotoelEMin       -0.61           % photo electron energy range and mesh
PhotoelEMax        1.29
DeltaPhotoelE      0.005
KsiCor             0.25           % spin-orbit parameter = 2 Delta / 3
ReVmtz            -0.61604        % zero of muffin-tin potential
OmegaMin          26.3           % photon energy range and mesh
OmegaMax          27.5
DeltaOmega         0.005
UnscreenedWeight 0.              % mixing parameter for screening
SlaterRkScale      0.            % possible scaling of Coulomb integrals
BasisEmin         -1.            % range for searching for trial orbitals
BasisEmax          1.
WithRefl           1             % if = 0  atomic calculation (rho = 0)
```

Output files

- A lot of information is written on screen.
It seems useful to redirect the screen output to some file.
`./mcms > output`

- if `rhochi.dat` exists, it is taken as input.
If not, it is output. Contains reflectivity data.

- `spectrum.dat` is the main spectrum output file.
The meaning of the columns is given in the first line:

`# omega [eV], Iiso=Ix+Iy+Iz, Ix, Iy, Iz, I-, I+, omega+ecore [eV]`

`omega` = photon energy, `omega+ecore` = photoelectron energy.

- `specqqprime.dat` contains the full tensor of polarisation dependent cross section, i.e. $I_{qq'}$ with $q = 0, \pm 1$.
First column: photoelectron energy = omega+ecore[eV].
$I_{qq'}$ is in column number $3q + q' + 6$.

- `specmmprime.dat` contains $I_{mm'}$ the cross section projected on final state d-orbitals m (diagonal and off-diagonal terms)

m	-2	-1	0	1	2
orbital	ixy	iyz	$3z^2$-r^2	zx	x^2-y^2

First column: photoelectron energy = omega+ecore[eV].
$I_{mm'}$ is in column number $5m + m' + 14$.

Tutorial − L23-edge spectra of CaO

Already prepared (directory `Input`)

− potential files (from an LMTO band structure calculation):
`Ca, O, Ca_ch` (= fully screened core-hole potential).

− core wave function file   `ca_2p_ch`

− input file   `mcms.in`

CaO6 octahedron

• write an `instr.dat` file for a CaO6 octahedron

Choose `lmax = 3` for Ca.

CaO has rocksalt structure.   (FCC with Ca at (0,0,0), O at (.5,.5,.5)).

Lattice constant a = 4.81 Å = 9.09 a.u.

- check your cluster. You can run the program `instr2xyz` which reads `instr.dat` and generates `str.xyz` (=structure file in XYZ format and Å). The latter can be used in most visualization software.

  If you fail writing your own `instr.dat` *file, look up* `MoreInput`

- run the code to calculate a spectrum in the independent particle aprroximation (`SlaterRkScale 0.`)

```
./mcms > output
```

- have a look at the `output` file

- plot the isotropic XAS spectrum from `spectrum.dat`

- check for linear dichroism by comparing Ix, Iy, Iz
  e.g. $Iz - Ix$ in gnuplot: `plot 'spectrum.dat' using 1:($5-$3)`

- analyze and assign the peaks in terms of d-orbital symmetries by plotting various columns of `specmmprime.dat`. What do you expect from group theory?

Tetragonal distortion

- remove or rename `rhochi.dat`

- perform a tetragonal distortion of the structure, e.g. by some $+4\%$ in z and -2% in x and y (bond lengths 4.635 and 4.365 a.u.) Repeat all the analyses and explain the observations.

Go back to the undistorted CaO6 cluster

- compare the isotropic spectrum with experiment

Core-hole effect − final state rule

- try to improve the spectrum by using different core-hole potentials

– `AbsCHPotFile Ca` and `UnscreenedWeight 0.`
– `AbsCHPotFile Ca_ch` and `UnscreenedWeight 0.`
– `AbsCHPotFile Ca_ch` and `UnscreenedWeight 0.1`

- use `AbsCHPotFile Ca_ch` and `UnscreenedWeight 0.1`
and switch on the multiplet coupling (`SlaterRk 1.0`)

- plot the isotropic spectrum and compare with experiment

- analyze and assign the peaks in terms of d-orbitals by plotting various columns of `specmmprime.dat`

27-atom cluster

- rename `instr.dat_27` to `instr.dat`

- visualize this cluster

- calculate isotropic spectrum and compare with CaO6 cluster

Be careful to choose sufficiently fine energy meshes (both for photon ω and photoelectron ϵ) because the peaks get sharper with increasing cluster size (why?)