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Xu Junqing, Calogero R. Natoli, Peter Krüger, Kuniko Hayakawa, Didier Sébilleau, et al.. ES2MS: An interface package for passing self-consistent charge density and potential from Electronic Structure codes To Multiple Scattering codes. Computer Physics Communications, 2016, 203, pp.331-338. 10.1016/j.cpc.2016.02.031 . hal-01286225

HAL Id: hal-01286225

https://univ-rennes.hal.science/hal-01286225

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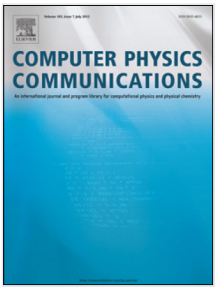

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PII: S0010-4655(16)30046-7
DOI: http://dx.doi.org/10.1016/j.cpc.2016.02.031
Reference: COMPHY 5890

To appear in: *Computer Physics Communications*

Received date: 4 October 2015
Revised date: 25 January 2016
Accepted date: 26 February 2016

Please cite this article as: X. Junqing, C.R. Natoli, P. Krüger, K. Hayakawa, D. Sébilleau, L. Song, K. Hatada, ES2MS: An interface package for passing self-consistent charge density and potential from Electronic Structure codes To Multiple Scattering codes, *Computer Physics Communications* (2016), http://dx.doi.org/10.1016/j.cpc.2016.02.031

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ES2MS: An interface package for passing self-consistent charge density and potential from Electronic Structure codes To Multiple Scattering codes

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Abstract

We present an interface package, called ES2MS, for passing self-consistent charge density and potential from Electronic Structure (ES) codes To Multiple Scattering (MS) codes. MS theory is based on the partitioning of the space by atomic-size scattering sites, so that the code provides the charge densities and potentials for each scattering site. For pseudo potential codes, the interface solves Poisson equation to construct the all-electron potential on the radial mesh which is used to solve the transition operators (T-matrix) and Green's functions in MS codes. We show the algorithm of the interface and the example for X-ray absorption spectra of graphene.

Keywords: Multiple Scattering, VASP, self-consistent, Poisson equation

Program summary

Program Title: ES2MS-1.0
Catalogue identifier:
Programming language: Fortran 90, FORTRAN 77
Computer: Any
Operating system: Linux, Mac OSX, Windows
RAM: several hundred Mega Bytes
Classification: 7.2
External routines/libraries:
Subprograms used:
Nature of problem: reconstruction of full-potential for Multiple Scattering codes from external charge densities, data transformation between cartesian supercell mesh onto radial meshes of real space cluster
Solution method: The pseudo-potential and the all-electron charge density from a Projecter-Augmented-Wave electronic structure method (here: VASP) are read. Inside the augmentation spheres, the charge density is interpolated onto the radial mesh of the Multiple Scattering code. The all-electron full-potential is obtained by solving the Poisson equation with proper boundary conditions on the surface of the spheres as given by the pseudopotential. Outside the spheres, the charge density and potential are interpolated from the cartesian mesh onto the radial mesh. By rotating and shifting the coordinates of the cluster used in the Multiple Scattering code, the code finds the corresponding point in the unit cell of the Electronic Structure code.
Running time: a few tens seconds

1. Introduction

Multiple Scattering (MS) theory has been widely applied to the computations of electronic structures [1] and spectroscopies [2] of various systems, such as crystal, molecule, surface, alloy, and systems with defects and adsorbates. Conventionally, it relies on Muffin-Tin (MT) approximation where the potential is spherically symmetrized and confined within nonoverlapping spheres while taking a constant value in the interstitial region. However, the MT approximation cannot properly describe a great number of physical systems, ranging from open lattices to molecular systems with substantial anisotropy (e.g. systems of biological interest), to surfaces and interfaces. There have been many progresses for extension of the MS Theory to the full potential (FP) level [3, 4, 5, 6, 7]. Apart from MS codes, there are a variety of electronic structure (ES) codes such as WIEN2K [8], VASP (Vienna Ab initio Simulation Package) [9], ABINIT [10], etc, for generating self-consistent charge density and potential. The advantage of these codes is that these are very specialized for the ground-state property, so that the calculation of the electronic structure in ground state is very efficient. On the other hand, for the calculation of the core electron spectroscopies and Green's functions which requires the right energy dependence, MS codes are very accurate and efficient.

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With the present ES2MS interface program, we combine the advantages of both approaches, by passing the charge density and potential of ES codes to MS codes. In this first version of ES2MS, the choice of the ES method is limited to the VASP code which uses the plane-wave Projector Augmented Wave (PAW) method.

Further, we developed a module to construct mixed potential and charge density from several ES output files. Several sets of ES output files can be used for constructing potentials and densities of inhomogeneous systems. This is useful for studying large systems, such as nanostructures or adsorbed molecules on surfaces, and generally for taking account of core-hole effects in core-level spectroscopy. For example, for a case of X-ray absorption in solid, the charge density and potential is separated in the following two regions, 1) near the absorbing atom, affected by the core-hole and 2) far from the absorbing atom, where the potential is almost the same as in ground state. This situation can be reproduced by using two sets of output of ES calculations, one with the core-hole in a big supercell and another one with a small unit cell for ground state. Thus we can realize a reasonable situation for real-space calculations with very large clusters. The detail of this treatment is described in Sec. 3.2.3.

2. Programming details

2.1. Overview of the software structure

The ES2MS package is organized as detailed in Fig. 1. The main directory "es2ms" includes all subroutine files while "es2ms_mod" defines all public variables and constants in modules. Main subroutines are in the main directory "es2ms". The subdirectory "common_sub" includes some small subroutines, which are not specific to ES2MS package, such as those for calculating the rotation matrix between two vectors, generating spherical harmonics, etc. On the other hand, subdirectory "atom" includes subroutines performing atomic calculations for adding a core-hole. For atomic calculations, subroutines previously written by A. L. Ankudinov, et al. [11] and T. Watanabe et al. [12] are used.

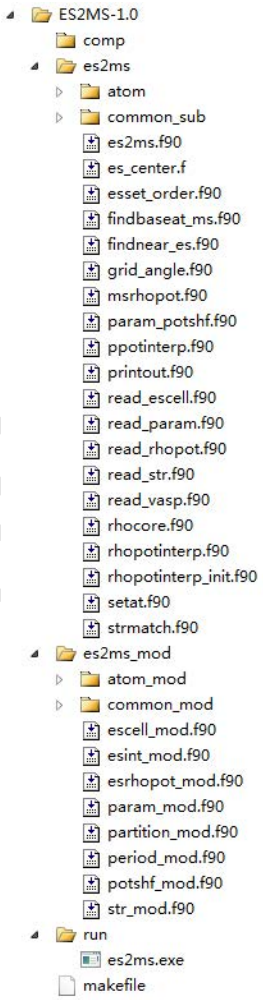

Figure 1: Directory tree of ES2MS package

2.2. Algorithm

The basic algorithm is simple and described in Fig. 2. More details are given in Sec. 2.3 and 3.2.

2.3. MS potential from PAW charge density

Plane-wave codes using the PAW method are popular because of their high accuracy and computational efficiency for total energy DFT calculations. In the PAW method [13], the all-electron Kohn-Sham potential is replaced by a pseudo potential inside the augmentation spheres around the nuclei. This pseudo potential coincides with the all-electron potential only in the space outside the augmentation spheres. However, for MS calculations the all-electron potential is required in all space, especially near the nuclei where the core orbital exhibits a large amplitude. Now we present a method for reconstructing the all-electron potential in the augmentation spheres from the knowledge of the all-electron charge density. The latter is commonly provided in PAW codes such as VASP [9], which we have used here. As the calculation of a local or semi-local exchange correlation potential from the charge density is straightforward, we only explain how to obtain the all-electron Hartree potential.

The mathematical problem is to find the regular solution of the Poisson equation inside an (augmentation) sphere S of radius r_c, with the Dirichlet boundary condition on the sphere, i.e. we want to solve

$$\nabla^2 V(\mathbf{r}) = -4\pi\rho(\mathbf{r})$$

for $r < r_c$, given the charge density ρ for all points inside S and the potential V on the surface ($r = r_c$). We introduce the function

$$W(\mathbf{r}) \equiv \int_S \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}\, d\mathbf{r}',$$

which satisfies the Poisson equation but, in general, not the boundary condition. $W(\mathbf{r})$ can easily be calculated in

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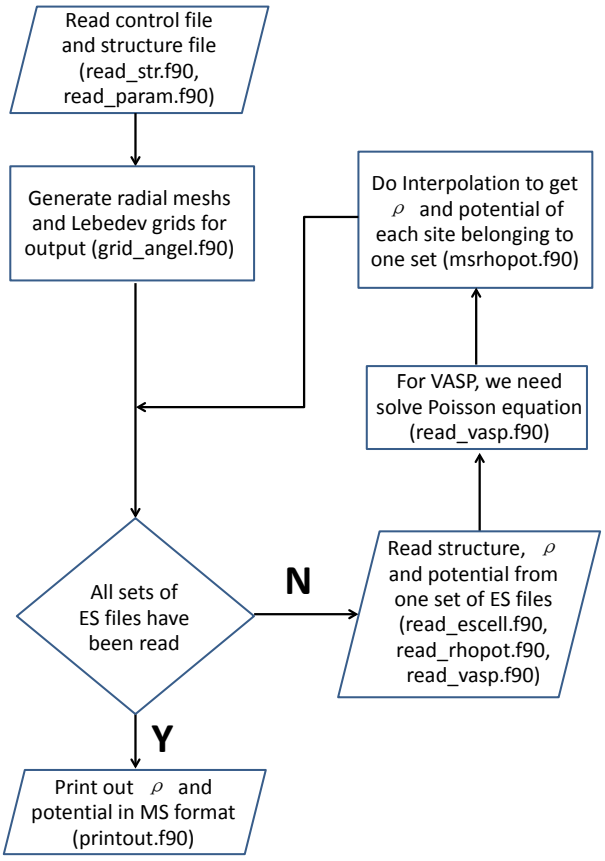

Figure 2: A schematic of algorithm of ES2MS. Inside brackets, the corresponding fortran files are shown. ρ represents charge density.

a spherical harmonic basis,

$$W(r,\hat{\mathbf{r}}) = \sum_L \omega_L(r) Y_L(\hat{\mathbf{r}}),$$

$$\omega_L(r) = \int_0^{r_c} \frac{r_<^l}{r_>^{l+1}} \rho_L(r') 4\pi r'^2 dr',$$

$$\rho_L(r) = \int Y_L^*(\hat{\mathbf{r}}) \rho(r,\hat{\mathbf{r}})\, d\hat{\mathbf{r}},$$

where $\hat{\mathbf{r}} = \mathbf{r}/r$. The angular integrals can be performed very accurately on a Lebedev mesh [14, 15]. The general solution of the Poisson equation is the sum of a particular solution, such as W, and the general solution of the corresponding homogeneous (i.e., Laplace) equation. The latter solution is $\sum_L C_L r^l Y_L(\hat{\mathbf{r}})$ for arbitrary coefficients C_L. By choosing $C_L = [v_L(r_c) - \omega_L(r_c)]/r_c^l$, where

$$v_L(r) = \int Y_L^*(\hat{\mathbf{r}}) V(r,\hat{\mathbf{r}})\, d\hat{\mathbf{r}},$$

the boundary conditions are satisfied, and so the final solution is given by

$$V(r,\hat{\mathbf{r}}) = \sum_L \left(\omega_L(r) + [v_L(r_c) - \omega_L(r_c)] \frac{r^l}{r_c^l} \right) Y_L(\hat{\mathbf{r}}) \,.$$

3. Input and output

Input and output files are described respectively in the first three subsections and the last two, respectively. The file names must be of the form "filenamestem.extension", and the "filenamestem", i.e., the part of the file name before the dot, must be the same for the last four files. For example, graphene.txt, graphene.xsf, graphene.pot, graphene.dens.

3.1. ES density and potential files (VASP only)

The ES2MS package reads the charge density and the pseudo Hartree potential provided by the VASP code and calculates the all-electron Hartree potential in the whole space for use in the MS code. The following three VASP output files are necessary: **AECCAR0** and **AECCAR2** which contain, the core and the SCF valence charge density, respectively; and **LOCPOT**, which contains the pseudo Hartree potentials inside the atomic spheres and the true potentials in the rest of the unit cell. The data in these files are stored on a regular three-dimensional grid of the unit cell. The above three files can be generated by the original VASP code when the following four lines are added in the input file **INCAR**:
LAECHG = .TRUE.
LADDGRID = .TRUE.
LVTOT = .TRUE.
LVHAR = .TRUE.

In an optional way of using the data on radial mesh, we need two other files, **RADCHGC** and **RADCHGV**, which contain the core and valence charge densities, expanded in spherical harmonics and stored on radial grids around each nucleus. To generate these two files, a small part of the VASP code should be modified (We have contacted to the VASP team to implement these changes into the standard VASP code). Only 11 lines of two source files altogether should be added or modified to print out radial core and valence charge density. (The detail is explained in README file.)

The VASP Hartree potential (in **LOCPOT**) is interpolated onto the radial meshes used in MS codes, in the region outside the augmentation spheres. The all-electron charge density is interpolated onto the MS mesh everywhere in the cluster. Further, the method described in Sec. 2.3 is applied to find the all-electron Hartree potentials inside the augmentation spheres.

Since in VASP code, the frozen core approximation is applied, i.e., the core charge density is the same as that of free atom in ground state, the core charge density can be easily generated by atomic calculation. The all-electron valence charge density inside the augmented sphere is obtained from **AECCAR2**. This way may introduce small errors, because interpolation for all-electron valence charge density inside the augmented sphere with the regular three-dimensional grids is less precise than with the radial grids. The errors can be considerably reduced by using "LADDGRID = .TRUE." in **INCAR**, which leads

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to the regular three-dimensional grids much finer than the usual grids [16]. Moreover, since only the SCF charge density and electrostatic potential are needed and this computation is light, the plane-wave cutoff energy can be chosen as a very high value, which leads to very fine regular three-dimensional grids. In reality, we have seen that with and without using **RADCHGC** and **RADCHGV**, the obtained all-electron charge densities are similar and electrostatic potentials are nearly the same. As checked, when we applied the SCF all-electron charge density and potential obtained with and without using **RADCHGC** and **RADCHGV** to compute the X-ray absorption spectra of graphene by Full-Potential Multiple Scattering theory [7], respectively, the two results are nearly the same. Further checks may be needed for some particular physical issues where the all-electron valence charge density inside the augmented sphere varies very rapidly and its accuracy is very crucial.

To add a hole in a VASP calculation, we must set **ICORELEVEL** = 2 (see Ref. [17]).

The core-hole must be added in the first atom in the unit cell in **POSCAR** for this version of ES2MS. When there are **nesset** sets of ES files, numbered 1, 2, ..., k, ..., **nesset**, then set No. 1 must be located in the same directory as the **txt** and **xsf** files, namely in the working directory. All other sets must be put into individual subdirectory, i.e. set No. k must be in the subdirectory **./setk/**. More details are discussed in Sec. 3.2.3.

3.2. Parameter file (.txt)

In this version, "&job" must be added at the beginning and the end, while at the end a line containing only "/" and an empty line are necessary.

3.2.1. General parameters

- **ES_type**: the type of ES code. By default, it is set to **'vasp'**.

- **na**: number of atoms in the cluster or in the unit cell. **na** can also be decided automatically by the number of atoms listed in the structure input file (**.xsf**), if **na** has not been given.

- **rchg_vasp**: by default, it is **.false.**. If **.true.**, the VASP output files **RADCHGC** and **RADCHGV** will be used. Otherwise, these two files will not be used and the ES2MS program will generate the core and valence charge densities inside the augmented sphere using the VASP output file AECCAR2.

- **nspecies_set**: an array of integers. When **rchg_vasp** is **.false.**, this array must be given by users. It provides numbers of atomic species of every set of VASP files (set No. 1, 2, ..., k, ..., **nesset**, if there are **nesset** sets of VASP files).

- **rcore_species**: an array of radii (always in atomic unit). When **rchg_vasp** is **.false.**, this array must be given by users. The size of this array is the same as the sum of the numbers of atomic species for all sets of VASP files. The number of atomic species of one set of VASP files should be consistent with the corresponding VASP input file POSCAR. For example, if set No. 1 and 2 of VASP output files are generated by two VASP calculations of ground-state graphene and graphene supercell with a core-hole, respectively, **nspecies_set(1)** and **nspecies_set(2)**, which are the numbers of atomic species of set No. 1 and 2, will be 1 and 2, respectively, since the carbon having a core-hole should be treated as a special atomic species in VASP code. Therefore, the size of the array **rcore_species** will be 3. The value of a particular element of the array **rcore_species** should be equal to the cutoff radius of the pseudo potential of the corresponding atomic species, which is named as **RCORE** in the VASP input file **POTCAR**.

- **silent**: by default, it is **.true.**. If **.false.**, the program will print more information.

- **unit_len**: if **ang** (default value), the unit for coordinates is Ångstrom; otherwise, atomic units are used.

3.2.2. Parameters for the radial and angular grids

For radial grids, the linear logarithmic mesh, $\rho = \alpha\, r + \beta \ln r$, is used for MS codes, and details are given in Ref. [7]. For angular grids, the Lebedev grids [14] are used during the process of reconstructing the charge density and potential.

- **kmax_ratio**: a parameter to increase or reduce the radial grids. For practical calculations, we recommend to use the default value - 0.8, so that the number of radial points is reduced by this factor from a number calculated by program.

- **alpha_all**, **beta_all**: giving these two parameters will set α and β of all sites (atoms and empty cells) as **alpha_all** and **beta_all**, respectively. By default, β of all sites are 1.0, and α of each site is calculated separately by the program.

- **lmax_es**: the maximum value of the orbital angular momentum used to reconstruct the density and the potential from the ES codes. The default value is 6.

- **ld_es**: the parameter of the Lebedev grid used to reconstruct the density and the potential from the ES codes. The default value is 350.

In outputs of ES2MS program, the charge density and potential are represented in angular momentum by expansion of the real spherical harmonics. For the reason of accuracy, we recommend to use **lmax_es** bigger than $lmax$, which is the maximum value of the orbital angular momentum of MS codes.

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3.2.3. Partitioning parameters

The parameters below determine how to partition the structure used in MS codes to several parts, so that part No. i "belongs to" set No. i of ES files, that is to say, the potential and charge density of this part of the whole system will be reconstructed using set No. i of ES output files. In order to add a hole, the corresponding atom or the absorber must belong to the last set or set No. **nesset**. Except that the files of the set No. 1 should be put in the main directory as the **.txt** and **.xsf** files, the files of set No. k should be put in the subdirectory **./setk/**.

- **nesset**: number of sets of ES output files.
- **partition_mode**:
  - **0**: the set of ES output files to which an output atom belongs must be given by the user in the **xsf** file in the following way:
    SET
    2
    2
    2
    2
    1
    1
    1
    1
    1
    1
    The starting line must be **SET**, the number of lines of digits should not be smaller than parameter **na**.
  - **1**: the structure used in MS codes is partitioned, according to parameters **centset**, **rset** and **zset**, in the following way:
    centset, **rset** and **zset** are all arrays with **nesset**-1 elements. Their kth element corresponds to the central atom, the threshold of the distance to the central atom and the threshold of the z coordinate of the central atom of set No. k, respectively.
    Suppose the coordinate of an atom is (x,y,z), and r1 is the distance from the atom indexed by **centset(1)**. If r1 > **rset(1)** and $|z - z(\textbf{centset(1)})| >$ **zset(1)**, this atom belongs to set No. 1. The default values of **centset** are 1. The default values of **rset** and **zset** are negative values. Once all atoms belonging to set No. 1 have been decided, we repeat the above process for the remaining atoms to decide which atoms belong to set No. 2. In total, this process will be done **nesset**-1 times. By definition, set No. 1 and **nesset** are the outermost and innermost sets, respectively.
    For a better understanding, we show an example in Fig. 3, where the system is partitioned by three parts, rset(2) and zset(1) are both nonzero while rset(1) and zset(2) are both zero.

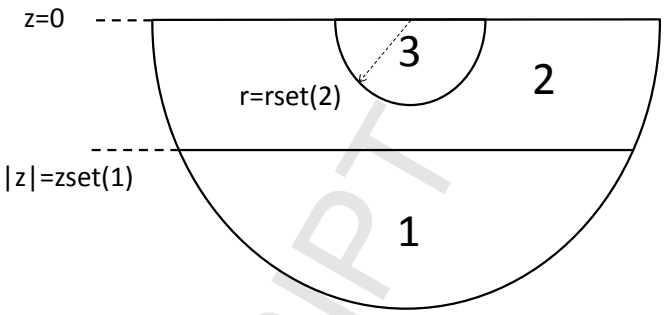

Figure 3: An example for partitioning the structure used in MS codes in three parts. rset(2) and zset(1) are both nonzero while rset(1) and zset(2) are both zero. More details about the way to partition a structure used in MS codes are given in Sec. 3.2.3.

3.2.4. match_mode

Since the origins and the direction of axis of Cartesian coordinate of the structures used in ES and MS codes, respectively, may be different, we need to shift and/or rotate the coordinate to match the structures used in ES and MS codes. The parameter **match_mode** determines the way how to make the structures used in ES codes and MS codes match.

- **match_mode=0**: rotation is forbidden so that two structures can match only by shifting. Shifting vectors of different sets of ES output files connect one atom in the structure used in ES codes to one atom in the structure used in MS codes. The indexes of these atoms in the structures used in ES codes and MS codes are controlled by the parameters - **fstat_es** and **fstat_ms**, respectively, which are one dimensional arrays whose values are initialized by 1 as default.
- **match_mode=1**: rotation will be done automatically. However, the structure of all sets should be the same.
- **match_mode=2**: rotation will be done automatically. Different sets can correspond to different crystals so that we can deal with systems with defects and adsorbates without requiring periodicity. An additional restriction is that **fstat_ms(i)** must belong to set i.

3.2.5. Parameters for adding a hole

In the VASP calculation with a hole, although an electron is added in the lowest unoccupied molecular orbital (LUMO), a core electron is not really removed in **RADCHGC**. Therefore, we should add a hole in ES2MS.

- **edge**: the edge name for core level spectrum, e.g. **'k '**, **'l1'**, **'l2'**, **'l3'**. **'k '** is the default.
- **nhole**: the fraction of hole to be added. The range is from 0.0 to 1.0. The default is 0.0.

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3.2.6. Shifting potential parameters

When a potential is generated by plane-wave ES codes, asymptotic behavior of the potential may not be reproduced correctly for low-dimensional systems in particular directions. Therefore vacuum level may not be defined well if the size of the supercell is not completely converged. In order to cure this condition, we shift the potential. As an example, let us consider a surface system. At certain point far from the surface in the vacuum space, the electrostatic potential should have very small value with positive sign. This asymptotic behavior is well reproduced in MS codes. In plane-wave ES codes, e.g., VASP, we have to deal with a surface system using slab model, it means we have to add a thick vacuum space above the surface in the supercell. However, in the case of graphene even with large thickness, e.g., 15 Å, the electrostatic potential at a point far from the surface, e.g., 7.5 Å, is -2eV, it is negative and its absolute value is not so small. To make the definitions of vacuum levels in MS codes and ES codes the same, we define the electrostatic potential of a point far from the surface as zero. When we study bulk systems, it is not necessary to shift the potential.

- **potshf_mode=0**: do nothing (default value).
- **potshf_mode=1**: shift is controlled by the parameters **essetvcm, essetfst**, and **refp_first** in the following way:
  - **essetvcm>0**: for every set of ES output files, the potential at point **refp_first** is set to zero.
  - **essetvcm=0**: the potential of set **essetfst** at **refp_fst** is treated as the reference potential, while the potentials of all the other sets at point **refp_fst** are fixed to this reference potential.
- **potshf_mode=2**: shift is controlled by the parameters **essetvcm, essetfst, refp_first**, and the two arrays - **set1_potshf** and **set2_potshf**, in the following way:

  if **essetvcm** > 0, the potential of set **essetvcm** at point **refp_fst** will be shifted to vacuum level. If **essetvcm** is zero, potential of set **essetfst** is kept unchanged. The potential of set **set1_potshf(i)** (1<= i <=**nesset**-1) at **refp_potshf(i)** is treated as the reference potential, so the potential of set **set2_potshf(i)** (1<= i <=**nesset**-1) at **refp_potshf(i)** is fixed to this reference.
- **potshf_mode=3 (4)**: similar to **potshf_mode=1 (2)**, but we shift the pseudo potential before solving the Poisson equation. In principle, it should be better than **potshf_mode=1 (2)**. Physically, the reference points should be outside the atomic spheres where pseudo potential is the same as the all-electron one for **potshf_mode** $\neq$ **0**.

3.3. Structure file (.xsf)

Every set of parameters must start with a character string for recognition. In this version, all three strings **ATOMS**, **RADII**, and **LMAX** must be present. **ATOMS** is followed by atomic numbers and coordinates (for crystal, lattice vectors are not needed). **RADII** lists the spherical radii while **LMAX** corresponds to the maximum l of the angular momentum expansion of each site. Additionally, user can arrange the partitioning which is discussed in Sec. 3.2.2 by specifying the corresponding set for each atom after the string **SET**. The radial mesh parameters α and β can be set for each atom by specifying the values after the strings **ALPHA** and **BETA**, respectively.

3.4. The potential file (.pot)

The first line contains an integer number **na**. The remaining lines contain **na** blocks of potential data, one for each atom. A potential data block starts with a first line which repeats the information on this atom given in the structure file, i.e. the atomic number and the coordinates (cartesian, Ångstrom units). This is followed, on the same line, by three integers: **nr**, *lmax* and **na_protp** whose explanations are given as follows.

nr is the number of radial mesh points, **na_protp** is the prototypical atom.

The potential V is expanded as

$$V(\mathbf{r}) = \sum_{l=0}^{lmax} \sum_{m=-l}^{l} \mathcal{Y}_{lm}(\hat{\mathbf{r}}) V_{lm}(r),$$

where $\mathbf{r}$ is the position vector relative to the nucleus, $r = |\mathbf{r}|$, lm are the angular momentum quantum numbers, and $\mathcal{Y}_{lm}$ are real spherical harmonics in the usual Condon-Shortley phase convention. Here we only consider non spin-polarized systems.

After this information line, the potential data is listed in the following format. Each line corresponds to a radial mesh point r_i for $i = 1$ to nr. The first column is r, and all other columns are $rV_{lm}(r)$. In the simplest case of a a spherically symmetric potential ($lmax = 0$), only one component, $rV_{00}(r)$ is written and the potential is $V(\mathbf{r}) = V_{00}(r)/\sqrt{4\pi}$. For r and rV, atomic Rydberg units are used, i.e. lengths are given in a.u.= 0.529 Å and energies in Ryd. The format for the floating point numbers r and rV is "(1PE16.9,X)" which represents single precision numbers without loss of precision.

A sample output file is given in the following:

```
5359
 6 0.0000000E+00 0.0000000E+00 0.0000000E+00 143 3 1
 7.566616203E-06 -4.253833332E+01
 7.566616203E-06 -3.303262727E-16
 7.566616203E-06 -8.148048059E-15
 7.566616203E-06 -2.972936454E-15
 7.566616203E-06  0.000000000E+00
    ......
```

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Theoretically, when $r \to 0$, $rV_{00} = \sqrt{4\pi} rV = -\sqrt{4\pi} \times 2 \times 6 \approx -42.5388924217$. In the above sample output file, for r=7.566616203E-06, rV_{00}=-42.53833332, it is close to the theoretical value.

3.5. The charge density file (.dens)

This file contains the charge densities of all the atoms in the order as given in the structure file. The format is exactly the same as that of the potential file (see the above subsection) except that in place of the potential $[rV_{lm}(r)]$, the multipole components $\rho_{lm}(r)$ of the charge density are written. The definition is

$$\rho(\mathbf{r}) = \sum_{lm} \mathcal{Y}_{lm}(\hat{\mathbf{r}}) \rho_{lm}(r).$$

The electronic charge inside a sphere of radius R is given by

$$Q(R) = \sqrt{4\pi} \int_0^R dr r^2 \rho_{00}(r) \ .$$

In the simplest case of a non spin-polarized calculation and a spherically symmetric charge density ($lmax = 0$), only one component, $\rho_{00}(r)$, is written and the charge density becomes $\rho(\mathbf{r}) = \rho_{00}(r)/\sqrt{4\pi}$.

4. Installation

The ES2MS package can be readily installed under the Linux operating system, as shown in the following. We have not tested the package on Macintosh or Windows operating systems, but we expect installation to be rather straightforward also in these cases.

- uncompress the compressed file
- enter the created directory
- type "make" if your Linux system has gfortran compiler, or "make FCOMP=ifort" if Intel Fortran compiler exists.

The executable file will be generated in the subdirectory **./run/** and named as "es2ms.exe".

5. Examples - real-space calculations

We have performed a ground-state calculation of graphene and an excited-state calculation of a 4×4×1 graphene supercell with a core-hole with the VASP code. The plane-wave cut-off energy is 680 eV for both. When importing the VASP potentials to the real-space cluster calculations, we use the final state potential only for atoms not further away from the absorbing site than some distance R, of the order of half the supercell dimension. For atoms beyond R, the ground-state VASP potential is used. In this way the periodic repetition of core-holes, which is an artefact of k-space methods (such as VASP) is avoided and convergence of the final results as a function of the VASP supercell size is very efficient. Fig. 4 shows this strategy for constructing potential.

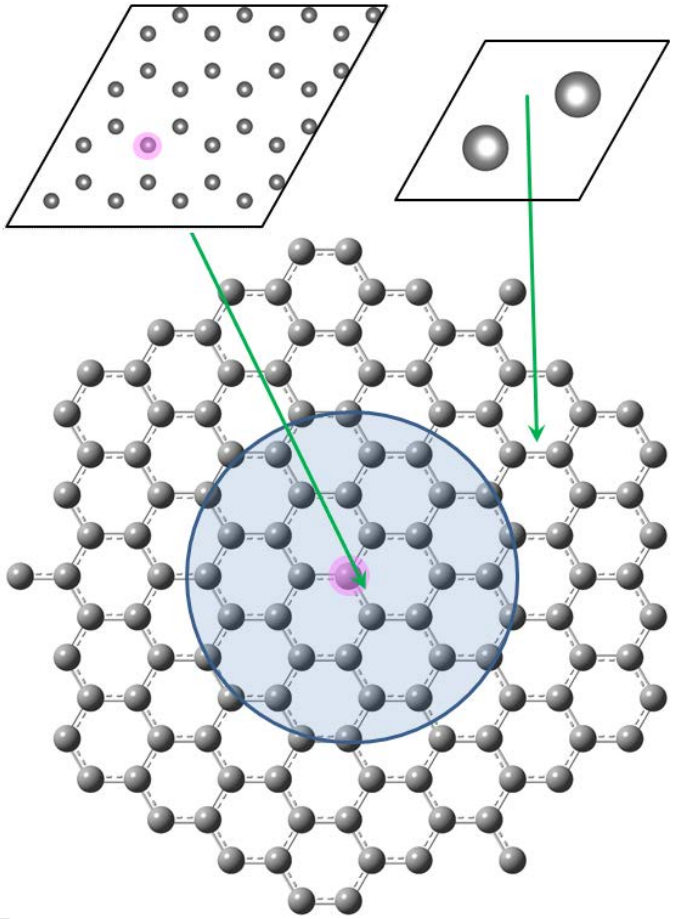

Figure 4: Schematic of the strategy for constructing the potential of a graphene cluster with a core-hole from two VASP potentials. The potential of the cluster inside the blue region is constructed from the excited-state VASP potential of a 4×4×1 graphene supercell with a core-hole, while the potential outside is constructed from the ground-state VASP potential. The carbon atom where a core-hole is colored in pink.

The txt file is:

```
&job
na = 5359,
nspecies_set = 1,2,
rcore_species = 1.1,1.1,1.1,
edge = "k ",
nhole = 1.0,
partition_mode = 1,
nesset = 2,
rset = 5.0,
potshf_mode = 3,
essetvcm = 2,
refp_fst = 0.0,0.0,7.5,
match_mode = 1,
fstat_ms = 1,1,
fstat_es = 1,1
/
```

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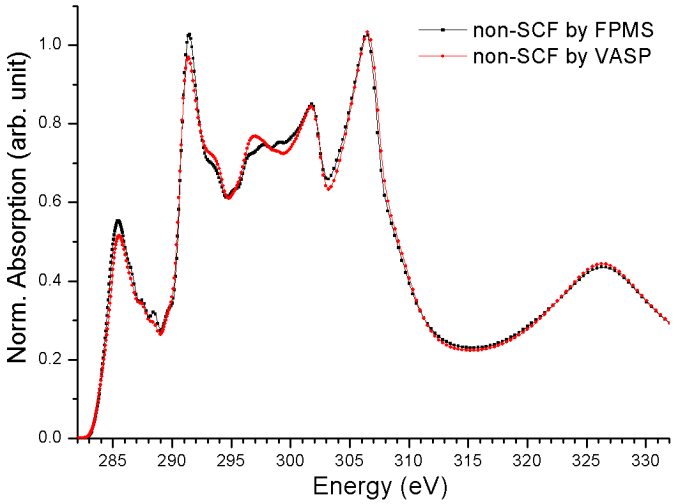

Figure 5: Calculated Carbon K-edge X-ray absorption spectra of graphene using different potentials. "non-SCF by FPMS" ("non-SCF by VASP") corresponds to the ground-state non-self-consistent potential generated by FPMS (VASP) code [7]. The spectra are aligned such that the π^* peak is at 285.5 eV.

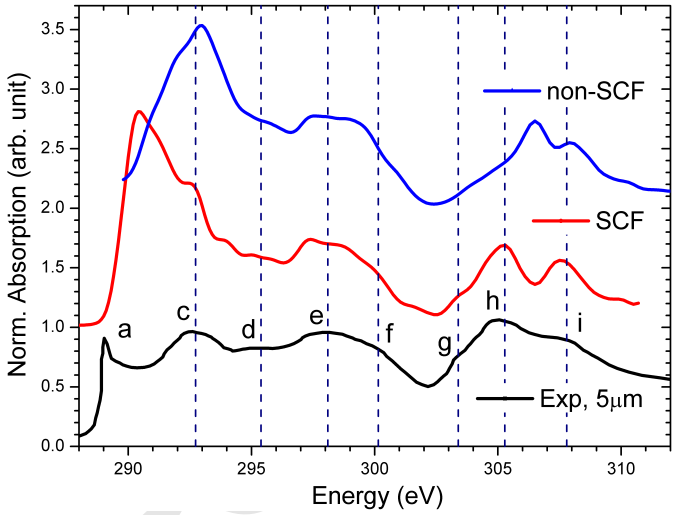

Figure 6: Calculated Carbon K-edge X-ray absorption spectra of a diamond cluster of radius 18 Å by FPMS code using non-SCF (self-consistent field) and SCF potentials, respectively. The SCF potential is generated by VASP code and reconstructed by ES2MS package. The experimental spectra is taken from Ref [19].

(An empty line must be put here.)
The xsf file is:

```
ATOMS
6    0.00000   0.00000   0.00000
0   -0.35604  -0.61668  -1.20000
0   -0.35604   0.61668  -1.20000
0   -0.35604  -0.61668   1.20000
0   -0.35604   0.61668   1.20000
0    0.71208   0.00000  -1.20000
0    0.71208   0.00000   1.20000
6    1.42416   0.00000   0.00000
6   -0.71208  -1.23336   0.00000
6   -0.71208   1.23336   0.00000
     ..... (5347 lines are omitted)
6  -29.90736   0.00000   0.00000
6   29.90736   0.00000   0.00000
RADII
0.95
0.9
0.9
0.9
0.9
0.9
0.9
0.95
0.95
0.95
     ..... (5347 lines are omitted)
0.95
0.95
LMAX
3
3
3
3
3
3
3
3
3
     ..... (5347 lines are omitted)
3
3
```

The computing time of the ES2MS process for the above calculation is less than 8 seconds for the executable program compiled by Intel Fortran on Linux operating system, and 12 seconds for gfortran compiler. The chipset is Intel Xeon E5-2609.

The resulting potential is used to calculate the polarized Carbon K-edge X-ray absorption spectra (XAS) of graphene by the FPMS code with the recently developed full-potential multiple scattering (FPMS) theory with space-filling cells [7]. In the FPMS method, space is partitioned by non-overlapping space-filling cells or Voronoi polyhedra, so that the radii in the **xsf** file are radii of the spheres enclosing the Voronoi polyhedra. When a Voronoi polyhedron does not contain any atom or is in the interstitial region but still contains charge density, it is called empty cell (EC) and its atomic number is set to zero for convenience. The resulting spectra and calculated spectra of some other systems, e.g., graphene edge and graphene oxide, can be found in Ref. [18]. A good agreement with experiments is achieved all the time.

Figure 5 shows two calculated Carbon K-edge X-ray absorption spectra of a graphene cluster, of radius 25 Å, by the FPMS code, using ground-state non-self-consistent potentials, which are reconstructed by ES2MS code from

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the VASP calculation of the infinite graphene and by the FPMS code directly, respectively. Since both non-self-consistent potentials are generated from the superposition of atomic charge densities, they should be nearly the same. The two results are quite similar, so that the reliability of our ES2MS code is ensured. The differences can be attributed to the differences between potentials of scattering sites near the boundary of the cluster.

Figure 6 shows the calculated Carbon K-edge X-ray absorption spectra of a diamond cluster of radius 18 Å by FPMS code using non-SCF (self-consistent field) and SCF potentials, respectively. The SCF potential is generated by VASP code and reconstructed by ES2MS package. It is clear that the SCF result agrees better with the experimental data [19] than the non-SCF result. In our previous work [18], we have found SCF potential to be important for Carbon and Oxygen K-edges of X-ray absorption spectra of graphene and graphene oxide. Therefore, ES2MS package can be quite useful for obtaining SCF potentials to calculate Green's functions in MS calculation, which are essential to compute various spectroscopies, especially for light elements.

Acknowledgements

K. H. acknowledges a funding of the European FP7 MS-BEEM (Grant Agreement No. PIEF-GA-2013-625388). Parts of this work have been funded by European FP7 MSNano network under Grant Agreement No. PIRSES-GA-2012-317554, by COST Action MP1306 EUSpec, by the National Natural Science Foundation of China (U1232131, 11375198), by the Science Fund for Creative Research Groups of the NSFC (11321503) and by JSPS KAKENHI Grant Number 25887008.

References

[1] H. Ebert, D. Ködderitzsch, J. Minár, Reports on Progress in Physics 74 (9) (2011) 096501.
[2] D. Sébilleau, R. Gunnella, Z. Wu, S. Di Matteo, C. Natoli, Journal of Physics: Condensed Matter 18 (9) (2006) R175.
[3] A. Williams, et al., Journal of Physics C: Solid State Physics 7 (1) (1974) 37.
[4] A. Gonis, W. H. Butler, Multiple scattering in solids, Springer, 2000.
[5] K. Hatada, K. Hayakawa, M. Benfatto, C. R. Natoli, Phys. Rev. B 76 (6) (2007) 060102.
[6] K. Hatada, K. Hayakawa, M. Benfatto, C. R. Natoli, J Phys Condens Matter 21 (10) (2009) 104206.
[7] K. Hatada, K. Hayakawa, M. Benfatto, C. R. Natoli, J Phys Condens Matter 22 (18) (2010) 185501.
[8] P. Blaha, K. Schwarz, G. Madsen, D. Kvasnicka, J. Luitz.
[9] G. Kresse, D. Joubert, Physical Review B 59 (3) (1999) 1758.
[10] X. Gonze, J.-M. Beuken, R. Caracas, F. Detraux, M. Fuchs, G.-M. Rignanese, L. Sindic, M. Verstraete, G. Zerah, F. Jollet, et al., Computational Materials Science 25 (3) (2002) 478–492.
[11] A. Ankudinov, S. Zabinsky, J. Rehr, Computer physics communications 98 (3) (1996) 359–364.
[12] T. Watanabe, M. Natori, T. Oguni, Fortran 77 ni yoru schi keisan sofutowea, Maruzen, Japan, 1989.
[13] P. E. Blöchl, Physical Review B 50 (24) (1994) 17953–17979.
[14] V. Lebedev, USSR Computational Mathematics and Mathematical Physics 15 (1) (1975) 44–51.
[15] V. Lebedev, D. Laikov, A quadrature formula for the sphere of the 131st algebraic order of accuracy, MAIK Nauka/Interperiodica, 1999.
[16] http://cms.mpi.univie.ac.at/vasp/guide/node142.html.
[17] http://cms.mpi.univie.ac.at/vasp/vasp/ICORELEVEL_tag_core_level_shifts.html.
[18] J. Xu, P. Krüger, C. R. Natoli, K. Hayakawa, Z. Wu, K. Hatada, Phys. Rev. B 92 (2015) 125408.
[19] Y. K. Chang, H. H. Hsieh, W. F. Pong, M. H. Tsai, F. Z. Chien, P. K. Tseng, L. C. Chen, T. Y. Wang, K. H. Chen, D. M. Bhusari, et al., Physical Review Letters 82 (26) (1999) 5377.

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Program title: ES2MS-1.0

Catalogue identifier: AFAB_v1_0

Program summary URL: http://cpc.cs.qub.ac.uk/summaries/AFAB_v1_0.html

Program obtainable from: CPC Program Library, Queen's University, Belfast, N. Ireland

Licensing provisions: Standard CPC licence, http://cpc.cs.qub.ac.uk/licence/licence.html

No. of lines in distributed program, including test data, etc.: 3351816

No. of bytes in distributed program, including test data, etc.: 82576761

Distribution format: tar.gz

Programming language: Fortran 90, FORTRAN 77.

Computer: Any.

Operating system: Linux, Mac OSX, Windows.

RAM: Several hundred Mega Bytes

Classification: 7.2.

Nature of problem:
Reconstruction of full-potential for Multiple Scattering codes from external charge densities, data transformation between cartesian supercell mesh onto radial meshes of real space cluster.

Solution method:
The pseudo-potential and the all-electron charge density from a Projecter-Augmented-Wave electronic structure method (here: VASP) are read. Inside the augmentation spheres, the charge density is interpolated onto the radial mesh of the Multiple Scattering code. The all-electron full-potential is obtained by solving the Poisson equation with proper boundary conditions on the surface of the spheres as given by the pseudopotential. Outside the spheres, the charge density and potential are interpolated from the cartesian mesh onto the radial mesh. By rotating and shifting the coordinates of the cluster used in the Multiple Scattering code, the code finds the corresponding point in the unit cell of the Electronic Structure code.

Additional comments:
!!!!! The distribution file for this program is over 82 Mbytes and therefore is not delivered directly when download or

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Email is requested. Instead a html file giving details of how the program can be obtained is sent. **!!!!!**

Running time:
A few tens of seconds