

# RHOLM code

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In the quantum chemistry group of Oviedo University (Spain), PROMOLDEN code [1] was designed to perform the topological analysis of the electron density according to the quantum theory of atoms in molecules (QTAIM) (see Chapter 2 in [2]). Here, an auxiliary code of PROMOLDEN, which has been termed as RHOLM, is introduced. This code enables one to generate the QTAIM multipole moments and apply different methodologies described below (see also [2] and [3]).

A RHOLM run is driven through a set of commands which are specified in an input file. This file is composed by several lines of characters which are internally divided into keywords and variables. The input file is not subjected to any format, except that: (a) punctuation marks are not allowable so that different words should be separated at least by one blank space; and (b) each command should be written in a single line. Uppercase and lowercase letters can be used interchangeably, except when filenames are specified. Atomic units are used in both input and output files.

The input file is divided into two different sections. First section specifies some binary files generated by PROMOLDEN code which include the radial  $A_{lm}^{\Omega}(r)$  functions (see Chapter 2 in [2]) as well as .pdat files where PROMOLDEN stores some relevant variables. Second section includes those commands required for performing different calculations.

Some conventions are used in the description on the different commands. On the one hand, keywords are written in bold characters. On the other hand, data provided by the user are written in italic characters.

## 1 Commands in the first section of the input file

- **data** *filepdat*: Provides the name *filepdat* for a file that stores some relevant variables involved in a PROMOLDEN calculation (i.e., .pdat file type). This command is always the first one in the input file.
- **outputname** *fileout*: Provides the name *fileout* (without extension) for a general PROMOLDEN output file (i.e., *fileout.rhdat* file). Furthermore, this name is also used to label other data files which will be described in the next section.
- **rhholm** *filealminp*: Provides the name *filealminp* for a binary file that stores the radial  $A_{lm}^{\Omega}(r)$  functions. If  $\beta$ -spheres were used in the PROMOLDEN calculation, then this file only stores the radial  $A_{lm}^{\Omega}(r)$  functions for that regions in the atomic basins outside of these  $\beta$ -spheres.
- **brholm** *filealmbinp*: Provides the name *filealmbinp* for a binary file that stores the radial  $A_{lm}^{\Omega}(r)$  functions in the  $\beta$ -spheres.
- **end**: Indicates the end of the first section in the input file.

## 2 Commands in the second section of the input file

The commands included in the second section of the input file call to different modules and routines in RHOLM code. These commands can be classified as: (a) commands for obtaining the different multipoles; (b) commands for calculating the Coulomb energy between topological atoms using the multipolar expansion (ME) and the bipolar expansion (BE) from Salmon, Birss and Ruedenberg; (c) commands for using the multipole shifting (MM) method, which improved the convergence of the ME for electrostatic interactions between topological atoms; and (d) commands for performing rotations on the radial  $A_{lm}^{\Omega}(r)$  functions.

### 2.1 Commands for obtaining the different multipoles

- **calcqlm**: Obtains the QTAIM multipole moments as from the radial  $A_{lm}^{\Omega}(r)$  functions included in the *filealminp* file (see Section 1). If  $\beta$ -spheres were used in the PROMOLDEN calculation, then these multipoles correspond to  $Q_{lm}^{out}(\Omega)$ .
- **calcbqlm**: Obtains the QTAIM multipole moments  $Q_{lm}^{\beta}(\Omega)$  as from the radial  $A_{lm}^{\Omega}(r)$  functions included in the *filealmbinp* file (see Section 1).
- **calcqlmtot**: Obtains the total QTAIM multipole moments by adding  $Q_{lm}^{\beta}(\Omega)$  and  $Q_{lm}^{out}(\Omega)$ .
- **wrlm**: Writes the radial  $A_{lm}^{\Omega}(r)$  functions in a *fileout.num.rlm* file, where *fileout* is specified in the first section (see Section 1) and *num*= 1, 2, ... is an integer number which enables one to distinguish among different files generated by invoking this command several times.
- **wqlm**: Writes the QTAIM multipole moments  $Q_{lm}(\Omega)$  in a *fileout.num.qml* file, where *fileout* is specified in the first section (see Section 1) and *num*= 1, 2, ... is an integer number which enables one to distinguish among different files generated by invoking this command several times.
- **calcqnlm nmax**: Obtains the multipoles  $Q_{nlm}(\Omega)$  for the BE from Salmon, Birss and Ruedenberg until a maximum order  $n = nmax$  as from the radial  $A_{lm}^{\Omega}(r)$  functions included in the *filealminp* file (see Section 1). If  $\beta$ -spheres were used in the PROMOLDEN calculation, then these multipoles correspond to  $Q_{nlm}^{out}(\Omega)$ .
- **calcbqnlm nbmax**: Obtains the multipoles  $Q_{nlm}^{\beta}(\Omega)$  for the BE from Salmon, Birss and Ruedenberg until a maximum order  $n = nbmax$  as from the radial  $A_{lm}^{\Omega}(r)$  functions included in the *filealmbinp* file (see Section 1).
- **calcqnlmtot**: Obtains the total multipoles for the BE from Salmon, Birss and Ruedenberg by adding  $Q_{nlm}^{\beta}(\Omega)$  and  $Q_{nlm}^{out}(\Omega)$  until a maximum order  $n_{max} = \min(nmax, nbmax)$ .
- **wqnlm**: Writes the multipoles  $Q_{nlm}(\Omega)$  for the BE from Salmon, Birss and Ruedenberg in a *fileout.num.qnlm*, where *fileout* is specified in the first section (see Section 1) and *num*= 1, 2, ... is an integer number which enables one to distinguish among different files generated by invoking this command several times.

It should be noted that the multipole moments of the topological atoms do not include the nuclear charge.

## 2.2 Commands for calculating the Coulomb energy between topological atoms

- **calcelecme** *ltot neq1 neq2*: Calculates the Coulomb energy between non-equivalent topological atoms *neq1* and *neq2* using the ME until a rank *ltot*. This rank should satisfy the condition  $0 \leq ltot \leq maxl$ , where *maxl* is the maximum angular quantum number of the QTAIM multipoles.
- **autcalcme** *neq1 neq2*: Calculates the Coulomb energy between non-equivalent topological atoms *neq1* and *neq2* using the ME for the rank values  $ltot = 0, \dots, maxl$ , where *maxl* is the maximum angular quantum number of the QTAIM multipoles.
- **sfactor** *afactor*: Defines the scaling factor *afactor* for the EB from Salmon, Birss and Ruedenberg.
- **calcelecbe** *ntot ltot neq1 neq2*: Calculates the Coulomb energy between non-equivalent topological atoms *neq1* and *neq2* using the EB from Salmon, Birss and Ruedenberg until ranks *ntot* and *ltot*. The rank *ltot* should satisfy the condition  $0 \leq ltot \leq maxl$ , where *maxl* is the maximum angular quantum number of the QTAIM multipoles. In turn, the rank *ntot* should satisfy the condition  $0 \leq ntot \leq n_{max}$ , where  $n_{max} = \min(nmax, nbmax)$  (see Section 2.1).
- **autcalcbe** *maxn neq1 neq2*: Calculates the Coulomb energy between non-equivalent topological atoms *neq1* and *neq2* using the EB from Salmon, Birss and Ruedenberg for the values of the ranks  $ntot = 0, \dots, maxn$  and  $ltot = 0, \dots, maxl$ , where  $0 \leq maxn \leq n_{max}$  being  $n_{max} = \min(nmax, nbmax)$  (see Section 2.1) and *maxl* is the maximum angular quantum number of the QTAIM multipoles.
- **convelecbe** *ntot ltot convt neq1 neq2*: Calculates the Coulomb energy between non-equivalent topological atoms *neq1* and *neq2* using the EB from Salmon, Birss and Ruedenberg until a convergence criteria *convt* is satisfied. The electrostatic interaction between topological atoms is written as

$$E_{elec}(A, B) = \sum_{N=1}^{ntot+1} \sum_{n_A=0}^{N-1} \sum_{l_A m_A} \sum_{l_B m_B} Q_{n_A l_A m_A}(\Omega_A) \times T_{n_A l_A m_A (N-n_A-1) l_B m_B}(\vec{R}) Q_{(N-n_A-1) l_B m_B}.$$

This expansion is said to reach the *convergence* at a rank *N* when the energy difference among the ranks *N*, *N* - 1, *N* - 2 and *N* - 3 is lower than *convt*. The rank *ltot* should satisfy the condition  $0 \leq ltot \leq maxl$ , where *maxl* is the maximum angular quantum number of the QTAIM multipoles. In turn, the rank *ntot* should satisfy the condition  $4 \leq ntot \leq n_{max}$ , where  $n_{max} = \min(nmax, nbmax)$  (see Section 2.1).

## 2.3 Commands for using the MM method

- **shift** *ltot neq1 neq2*: Calls the SHIFT module for calculating the Coulomb energy between non-equivalent topological atoms *neq1* and *neq2* until a rank *ltot*, where  $4 \leq l \leq maxl$  being *maxl* the maximum angular quantum number of the QTAIM multipoles.
- **minimumshift**: Calls the MINIMUMSHIFT module for calculating the Coulomb energy between non-equivalent topological atoms.

- **compshift**: Calls the COMPSHIFT module for obtaining the total, truncation and shift errors (see [3]).

It should be noted that the MM method requires the use of  $\beta$ -spheres.

Commands involved in the SHIFT module:

- **convergent convt**: Convergence criteria *convt* for the different contributions to the Coulomb energy. The condition *conv* > 0 should be satisfied.
- **monomin mmin**: Integer minimum value *mmin* for the one-dimensional displacements along the direction determined by a vector that connects the nuclei from both non-equivalent topological atoms. The condition *mmin*  $\geq$  0 should be satisfied.
- **bimin bmin**: Integer minimum value *bmin* for the two-dimensional displacements on a plane that contains the nuclei from both non-equivalent topological atoms. The condition *bmin*  $\geq$  0 should be satisfied.
- **trimin tmin**: Integer minimum value *tmin* for the three-dimensional displacements. The condition *tmin*  $\geq$  0 should be satisfied.
- **monomax mmax**: Integer maximum value *mmax* for the one-dimensional displacements along the direction determined by a vector that connects the nuclei from both non-equivalent topological atoms. The condition *mmax*  $\geq$  *mmin* should be satisfied.
- **bimax bmax**: Integer maximum value *bmax* for the two-dimensional displacements on a plane that contains the nuclei from both non-equivalent topological atoms. The condition *bmax*  $\geq$  *bmin* should be satisfied.
- **trimax tmax**: Integer maximum value *tmax* for the three-dimensional displacements. The condition *tmax*  $\geq$  *tmin* should be satisfied.
- **monoincrement mincrem**: Determines a set of displacement vectors for the one-dimensional case. Let  $\vec{u}$  be a unitary vector along the internuclear direction. The minimum and maximum displacement vectors are given by  $\vec{c}_{min} = (mmin \times mincrem)\vec{u}$  and  $\vec{c}_{max} = (mmax \times mincrem)\vec{u}$ , respectively. The difference between two consecutive displacements is given by the real number *mincrem* that satisfies the condition *mincrem* > 0.
- **bincrement bincrem1 bincrem2**: Determines a set of displacement vectors for the two-dimensional case. Let  $\vec{u} = \vec{u}_x + \vec{j}u_y + \vec{k}u_z$  be a unitary vector along the internuclear direction. Let  $\vec{v} = \frac{1}{\sqrt{u_y^2 + u_z^2}}(\vec{j}u_z - \vec{k}u_y)$  be a unitary vector that is orthogonal to  $\vec{u}$ . The minimum and maximum displacement vectors are given by  $\vec{c}_{min} = bmin \times (bincrem1\vec{u} + bincrem2\vec{v})$  and  $\vec{c}_{max} = bmax \times (bincrem1\vec{u} + bincrem2\vec{v})$ , respectively. The difference between two consecutive displacements is given by  $\sqrt{bincrem1^2 + bincrem2^2}$ , where the real numbers *bincrem1* and *bincrem2* satisfy the conditions *bincrem1* > 0 and *bincrem2* > 0, respectively.
- **trincrement tincrem1 tincrem2 tincrem3**: Determines a set of displacement vectors for the three-dimensional case. Let  $\vec{u} = \vec{i}u_x + \vec{j}u_y + \vec{k}u_z$  be a unitary vector along the internuclear direction. Let  $\vec{v} = \frac{1}{\sqrt{u_y^2 + u_z^2}}(\vec{j}u_z - \vec{k}u_y)$  be a unitary vector that is orthogonal to  $\vec{u}$ . Let  $\vec{w} = \frac{1}{\sqrt{1 + u_x^2}}(\vec{i} - \vec{j}\frac{u_x u_y}{u_y^2 + u_z^2} - \vec{k}\frac{u_x u_z}{u_y^2 + u_z^2})$  be a unitary vector that is orthogonal to  $\vec{u}$  and  $\vec{v}$ . The minimum and maximum displacement vectors

are given by  $\vec{c}_{min} = tmin \times (tincrem1\vec{u} + tincrem2\vec{v} + tincrem3\vec{w})$  and  $\vec{c}_{max} = tmax \times (tincrem1\vec{u} + tincrem2\vec{v} + tincrem3\vec{w})$ , respectively. The difference between two consecutive displacements is given by  $\sqrt{tincrem1^2 + tincrem2^2 + tincrem3^2}$ , where the real numbers  $tincrem1$ ,  $tincrem2$  and  $tincrem3$  satisfy the conditions  $tincrem1 > 0$ ,  $tincrem2 > 0$  and  $tincrem3 > 0$ , respectively.

- **monoshift**: Calculates the Coulomb energy between the given topological atoms using the set of displacement vectors for the one-dimensional case. The commands **convergent**, **monomin**, **monomax** and **monoincrement** should be invoked before this command.
- **bishift**: Calculates the Coulomb energy between the given topological atoms using the set of displacement vectors for the two-dimensional case. The commands **convergent**, **bimin**, **bimax** and **bincrement** should be invoked before this command.
- **trishift**: Calculates the Coulomb energy between the given topological atoms using the set of displacement vectors for the three-dimensional case. The commands **convergent**, **trimin**, **trimax** and **trincrement** should be invoked before this command.
- **allbishift** *llin rinc*: Scans different directions on a plane determined by the orthonormal vectors  $\{\vec{u}, \vec{v}\}$  until achieve the convergence for the Coulomb energy between non-equivalent topological atoms. To this end, a set of angles  $\alpha = 0, \frac{\pi}{llin}, 2\frac{\pi}{llin}, \dots, (llin - 1)\frac{\pi}{llin}$  is defined, where  $llin > 0$  is an integer number. For each  $\alpha$  value, one defines the increments  $bincrem1 = rinc \times \cos(\alpha)$  and  $bincrem2 = rinc \times \sin(\alpha)$ , where  $rinc > 0$  is a real number. From these increments, a set of displacement vectors is defined in the same manner as in the **bincrement** command. The commands **convergent**, **bimin** and **bimax** should be invoked before this command.
- **alltrishift** *llin1 llin2 rinc*: Scans different directions determined by the orthonormal vectors  $\{\vec{u}, \vec{v}, \vec{w}\}$  until achieve the convergence for the Coulomb energy between non-equivalent topological atoms. To this end, two set of angles  $\beta = 0, \frac{\pi}{llin1}, 2\frac{\pi}{llin1}, \dots, (llin1 - 1)\frac{\pi}{llin1}$  and  $\alpha = 0, \frac{\pi}{llin2}, 2\frac{\pi}{llin2}, \dots, (llin2 - 1)\frac{\pi}{llin2}$  are defined, where  $llin1 > 0$  and  $llin2 > 0$  are integer numbers. For each value of  $\beta$  and  $\alpha$ , one defines the increments  $tincrem1 = rinc \times \sin(\beta)\cos(\alpha)$ ,  $tincrem2 = rinc \times \sin(\beta)\sin(\alpha)$  and  $tincrem3 = rinc \times \cos(\beta)$ , where  $rinc > 0$  is a real number. The commands **convergent**, **trimin** and **trimax** should be invoked before this command.
- **endshift**: Ends the commands involved in the SHIFT module.

Commands involved in the MINIMUMSHIFT module:

- **rem**: Indicates that the line is a comment without any command.
- **neq** *neq1 neq2*: Indicates the non-equivalent topological atoms *neq1* and *neq2* for calculating the Coulomb energy.
- **ltot** *ltot*: Maximum *ltot* rank in the ME. The condition  $0 \leq ltot \leq maxl$  should be satisfied, where *maxl* is the maximum angular quantum number of the QTAIM multipoles.
- **monomin** *mmin*: Integer minimum value *mmin* for the one-dimensional displacements along the direction determined by a vector that connects the nuclei from both non-equivalent topological atoms. The condition  $mmin \geq 0$  should be satisfied.

- **monomax** *mmax*: Integer maximum value *mmax* for the one-dimensional displacements along the direction determined by a vector that connects the nuclei from both non-equivalent topological atoms. The condition  $mmax \geq mmin$  should be satisfied.
- **monoincrement** *mincrem*: Determines a set of displacement vectors for the one-dimensional case. Let  $\vec{u}$  be a unitary vector along the internuclear direction. The minimum and maximum displacement vectors are given by  $\vec{c}_{min} = (mmin \times mincrem)\vec{u}$  and  $\vec{c}_{max} = (mmax \times mincrem)\vec{u}$ , respectively. The difference between two consecutive displacements is given by the real number *mincrem* that satisfies the condition  $mincrem > 0$ .
- **divisor** *divid*: The number of displacements for calculating the merit of the total error in the Coulomb energy between non-equivalent topological atoms (see Eq. 15 in [3]) is given by  $nprom = jmax/divid$  (or  $nprom = jmax/divid - 1$  if  $jmax/divid$  is odd), where  $jmax = mmax - mmin + 1$  and *divid* is an integer number that satisfies  $2divid \geq jmax$ .
- **endmshift**: Ends the commands involved in the MINIMUMSHIFT module.

Commands involved in the COMPSHIFT module:

- **rem**: Indicates that the line is a comment without any command.
- **neq** *neq1 neq2*: Indicates the non-equivalent topological atoms *neq1* and *neq2* for calculating the Coulomb energy.
- **ltot** *ltot*: Maximum *ltot* rank in the ME. The condition  $0 \leq ltot \leq maxl$  should be satisfied, where *maxl* is the maximum angular quantum number of the QTAIM multipoles.
- **monomin** *mmin*: Integer minimum value *mmin* for the one-dimensional displacements along the direction determined by a vector that connects the nuclei from both non-equivalent topological atoms. The condition  $mmin \geq 0$  should be satisfied.
- **monomax** *mmax*: Integer maximum value *mmax* for the one-dimensional displacements along the direction determined by a vector that connects the nuclei from both non-equivalent topological atoms. The condition  $mmax \geq mmin$  should be satisfied.
- **monoincrement** *mincrem*: Determines a set of displacement vectors for the one-dimensional case. Let  $\vec{u}$  be a unitary vector along the internuclear direction. The minimum and maximum displacement vectors are given by  $\vec{c}_{min} = (mmin \times mincrem)\vec{u}$  and  $\vec{c}_{max} = (mmax \times mincrem)\vec{u}$ , respectively. The difference between two consecutive displacements is given by the real number *mincrem* that satisfies the condition  $mincrem > 0$ .
- **energy** *exact*: *exact* is the Coulomb energy used as a reference, e.g., electrostatic energy between the given topological atoms calculated from PROMOLDEN.
- **outputname** *fileshift*: Provides the name *fileshift* for an output file that contains the original and shifted multipole moments.
- **endcshift**: Ends the commands involved in the COMPSHIFT module.

## 2.4 Commands for performing rotations on the radial $A_{lm}^{\Omega}(r)$ functions

- **rotmat**: Calls the ROTMAT module for rotating the radial  $A_{lm}^{\Omega}(r)$  functions by means of a rotation matrix  $\mathbf{R}$  in Cartesian coordinates.

- **rotvec**: Calls the ROTVEC module for rotating the radial  $A_{lm}^{\Omega}(r)$  functions around a  $z$  axis specified by the user. It should be noted that  $x$  and  $y$  axes are included in a plane perpendicular to the  $z$  axis, and their directions are arbitrary.
- **rot dip** (*inside|outside|total*): Calls the ROTDIP module for rotating the radial  $A_{lm}^{\Omega}(r)$  functions such that  $z$  axis is along the direction determined by the dipolar moment  $(-Q_{11}^{\eta}(\Omega), -Q_{1-1}^{\eta}(\Omega), Q_{10}^{\eta}(\Omega))$ , where  $\eta = \beta, out, total$  for *inside*, *outside* and *total*, respectively. It should be noted that  $x$  and  $y$  axes are included in a plane perpendicular to the  $z$  axis, and their directions are arbitrary.

Commands involved in the ROTMAT module:

- **ineq neq ... endineq**: Performs a rotation on the radial  $A_{lm}^{\Omega}(r)$  functions for the topological atom *neq*. The commands between **ineq** and **endineq** are
  - **file1** *rotm(1,1) rotm(1,2) rotm(1,3)*
  - **file2** *rotm(2,1) rotm(2,2) rotm(2,3)*
  - **file3** *rotm(3,1) rotm(3,2) rotm(3,3)*

where  $rotm(i,j)$  is the element at the  $i$ -row and  $j$ -column of the **R** matrix.

- **all ... endall**: Performs a rotation on all the radial  $A_{lm}^{\Omega}(r)$  functions. The commands between **all** and **endall** are
  - **file1** *rotm(1,1) rotm(1,2) rotm(1,3)*
  - **file2** *rotm(2,1) rotm(2,2) rotm(2,3)*
  - **file3** *rotm(3,1) rotm(3,2) rotm(3,3)*

where  $rotm(i,j)$  is the element at the  $i$ -row and  $j$ -column of the **R** matrix.

- **endrotmat**: Ends the commands involved in the ROTMAT module.

Commands involved in the ROTVEC module:

- **ineq neq rotv(1) rotv(2) rotv(3)**: Performs a rotation on the radial  $A_{lm}^{\Omega}(r)$  functions for the topological atom *neq*, where  $rotv(i)$  is the  $i$ th-Cartesian coordinate for the  $z$  axis after rotation.
- **all neq rotv(1) rotv(2) rotv(3)**: Performs a rotation on the all radial  $A_{lm}^{\Omega}(r)$  functions, where  $rotv(i)$  is the  $i$ th-Cartesian coordinate for the  $z$  axis after rotation.
- **endrotvec**: Ends the commands involved in the ROTVEC module.

Commands involved in the ROTDIP module:

- **ineq**: Performs a rotation on the radial  $A_{lm}^{\Omega}(r)$  functions for the topological atom *neq*.
- **all**: Performs a rotation on the all radial  $A_{lm}^{\Omega}(r)$  functions.
- **endrot dip**: Ends the commands involved in the ROTDIP module.

## References

- [1] A. M. Pendás, *PROMOLDEN code documentation* (2001).
- [2] C. J. F. Solano, *PhD Thesis* (2009).
- [3] C. J. F. Solano, A. M. Pendás, E. Francisco, M. A. Blanco and P. L. A. Popelier, *J. Chem. Phys.*, **132**, 194110 (2010).