MANUAL

WMPack –version 1.0

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Licensing

Publications of results obtained with the *WMPack* - version 1.0 software should cite the program and/or the article describing the program.

Abstract

WMPack is a computer program for generating input files and computing electronic energies by the WMS, W2X, W3X, and W3X-L multilevel methods. To use the WMS or W2X method in *WMPack*, one needs the *Molpro* program, and to use the W3X or W3X-L method in *WMPack*, one needs the *Molpro* and MRCC programs.

Table of Contents

Chapter One

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1. Introduction

WMPack is a perl program for generating input files and computing energies by the WMS, W2X, W3X, and W3X-L multilevel methods. *WMPack* stands for "Wuhan-Minnesota package". To use the WMS or W2X method in *WMPack,* one needs the *Molpro* program, and to use the W3X or W3X-L method in *WMPack* , one needs the *Molpro* and MRCC programs. Table 1 is a summary of all the scripts in *WMPack* .

Table 1. *Perl* scripts in *WMPack*

Scripts	Input file for the script	functionality
mWMS.pl	XYZ format with charge and spin	generate the *Molpro* input file for WMS
mWMS_gs.pl	*Gaussian 09* single-point energy output file	generate the *Molpro* input file for WMS
mWMS_go.pl	*Gaussian 09* geometry optimization output file	generate the *Molpro* input file for WMS
mWMS_mo.pl	*Molpro* geometry optimization output file	generate the *Molpro* input file for WMS
mW3X_gs.pl	*Gaussian 09* single-point energy output file	generate the *Molpro* input file for W3X
mW3XL_gs.pl	*Gaussian 09* single-point energy output file	generate the *Molpro* input file for W3X-L
mW3XL_mo.pl	*Molpro* geometry optimization output file	generate the *Molpro* input file for W3X-L
mW2X_gs.pl	Gaussian single-point energy output file	generate the *Molpro* input file for W2X
mW2X_mo.pl	*Molpro* geometry optimization output file	generate the *Molpro* input file for W2X
rWMs.pl	WMS *Molpro* output file	Compute the WMS energies

Chapter Two

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2. References for the *WMPack* Program

The recommended reference for the current version of the code is given below in three styles, namely in *J. Chem. Phys.* style, *J. Am. Chem. Soc.* style., and *Chem. Phys. Lett.* style.

J. Chem. Phys. style:

Y. Zhao and D. G. Truhlar, *WMPack -version 1.0* (Wuhan University of Technology & University of Minnesota, Minneapolis, 2018).

J. Amer. Chem. Soc. style:

Zhao, Y.; Truhlar, D. G. *WMPack -version 1.0*, Wuhan University of Technology & University of Minnesota: Minneapolis, 2018.

Chem. Phys. Lett. style:

Y. Zhao, D.G. Truhlar, *WMPack -version 1.0*. Wuhan University of Technology & University of Minnesota, Minneapolis, 2018.

Of course, the user should also give the *Molpro* or MRCC reference if and when those programs are also used and should give the *Gaussian* reference if one uses *Gaussian* to generate geometries.

In addition to giving references for the software, one should give references for the methods employed. The appropriate references are as follows:

WMS

Y. Zhao, L. Xia, X. Liao, Q. He, M. X. Zhao, and D. G. Truhlar, Extrapolation of High-Order Correlation Energies: The WMS Model, Phys. Chem. Chem. Phys., 2018, in press. doi.org/10.1039/C8CP04973D

W3X

B. Chan, L. Radom, A Cost-Effective Post-CCSD(T) Composite Procedure. J. Chem. Theory Comput. 2013, 9, 4769-4778.

W2X & W3X-L

B. Chan, L. Radom, W2X and W3X-L: Cost-Effective Approximations to W2 and W4 with kJ mol^{-1} Accuracy. J. Chem. Theory Comput. 2015, 11, 2109-2119.

Chapter Three

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3. General Program Description

WMPack is written in the *Perl* scripting language, and it consists of ten *Perl* scripts. As shown in Table 1, one can prepare a WMS geometry input file in the xyz format for the script, and one can also use a *Gaussian* or *Molpro* output file as the input file for one of the *WMPack* scripts. *WMPack* can generate an *Molpro* input file for the five composite multilevel methods, including WMS, W2X, W3X, and W3X-L. The users need to invoke the *Molpro* program to do the calculations for each components specified in the *Molpro* input file generated by *WMPack* . After the calculations are done, the user can use one of the *WMPack* script to calculate the composite energies.

Chapter 4 presents the theoretical background of all methods in this program. Chapter 5 summarizes the input files. Chapters 6 describes installation, and see Chapter 7 for a complete listing of all the files that compose the source code of *WMPack* . Chapter 8 presents the test jobs. Chapter 9 describes the computers and operating systems on which the code has been tested. Chapter 10 gives bibliography, and Chapter 11 is the revision history.

Chapter Four

4

4. Theoretical Background

This chapter describes the WMS Method and its comparison to W2X, W3X, and W3X-L.

4.1 Basis Sets

The basis sets that we have employed in the WMS method are shown in Table 2, with the corresponding references, in order of basis set size.

Table 2. Basis sets in the WMS method

Short name	Description	N^a	Ref.
jun-D	jun-cc-pV(D+d)Z ^{b}	73	1-4
wCVD	cc-pwCVDZ	78	5
jul-D	jul-cc-pV(D+d)Z^b	88	1-4
jul-D-DK	cc-pVDZ-DK for hydrogen, and aug-cc-pVDZ-DK for heavy atoms	88	4,6-8
T	cc-pVTZ	136	1-3
jun-T	jun-cc-pV(T+d)Z^b	163	1-4
jul-T	jul-cc-pV(T+d)Z^b	184	1-4
jul-T-DK	cc-pVTZ-DK for hydrogen, and aug-cc-pVTZ-DK for heavy atoms	184	4,6-8
wCVT	cc-pwCVTZ	187	5
T-F12	cc-pVTZ-F12	222	9

[a] *N* is the number of contracted basis functions for vinyl chloride C_2H_3Cl.

[b] For elements where a (D+d)Z or (T+d)Z basis does not, these bases sets aree dfeined as being the same as the corresponding DZ and TZ basis sets.

In the W2X, W3X, W3X-L methods, there are several basis sets that are not used in the WMS methods, and they are list in Table 3.

Table 3. Additional basis sets in the W2X, W3X, and W3X-L methods

Short name	Description	N^a	Ref.
D(NP)	cc-pVDZ without the polarization basis functions; NP = No Polarization	37	10
D(d)	cc-pVDZ for hydrogen, and aug-cc-pVDZ for heavy atoms	52	10
T(NP)	cc-pVTZ with no polarization functions	81	11
T(d)	cc-pVTZ with no polarization functions on hydrogen and the 2df functions for heavy atoms replaced by the d polarization functions taken from cc-pVDZ	106	10
CVD(2d)	*s* and *p* basis functions of cc-pCVDZ plus *d* basis functions of cc-pCVTZ	108	10
CVT(3d)	*s*, *p* and *f* basis functions of cc-pCVTZ plus *d* basis functions of cc-pCVQZ	217	10
jul-QZ	cc-pVQZ for hydrogen, and aug-cc-pVQZ for heavy atoms	334	7,12,13

$^a N$ is the number of contracted basis functions for vinyl chloride C_2H_3Cl.

4.2 Methodology and Theory of WMS

These WMS method is built on the following formula for the Born-Oppenheimer energy:

$$\begin{aligned} E(\text{WMS}) = {} & E(\text{CCSD(T)-F12b/jul-D}) + c_{\text{HF}}[\Delta E(\text{HF})] + c_{\text{CABS}}[\Delta E(\text{CABS})] \\ & + c_{\text{MP2}}[\Delta E(\text{MP2-cor})] + c_{\text{F12}}[\Delta E(\text{F12})] + c_{\text{CCSD}}[\Delta E(\text{CCSD-HO})] \\ & + c_{\text{(T)}}[\Delta E(\text{CCSD(T)-F12})] + \text{E}_{\text{CV}} + \text{E}_{\text{SRel}} + \text{E}_{\text{SO}} \end{aligned} \tag{1}$$

where

$$\Delta E(\text{X}) = \text{E(X/jul-T)} - \text{E(X/jul-D)} \tag{2}$$

The various methods X are explained below, the jul-D and jul-T basis sets are explained in Table 1, E_{CV} is the core-valence correlation energy, E_{SRel} is the scalar relativistic contribution, E_{SO} is vector relativistic contribution (which is labeled in the usual way as the spin-orbit (SO) term), and c_{HF}, c_{CABS}, c_{MP2}, c_{F12}, c_{CCSD}, $c_{\text{(T)}}$ and the parameters in E_{CV} have been optimized against the W4-17 database by minimizing the RMSE of the atomization energies in W4-17.

Details of how each of the terms in eq. (1) is calculated are given in the following subsections.

4.2.1 CBS Extrapolation. Two of the terms (explained below) in eq 1 involve extrapolating to the CBS limit by using the two-point power-law formula:[14]

$$E(n) = E^{CBS} + A/n^{\alpha} \tag{3}$$

where n is 2 for double zeta and 3 for triple zeta, and α is a parameter.

4.2.2 Hartree-Fock Components. In the WMS scheme, the HF components include the complementary auxiliary basis singles (CABS)[15] correction as adopted in the Wn-F12[16,17] and WnX[10,18] models, and the canonical HF energy and the CABS energy are treated as separate terms (X = HF and X = CABS) in eq. (1).

4.2.3 Explicitly Correlated Calculations. MP2 and CCSD calculations with F12 and CCSD(T) calculations with F12b suffixes are explicitly correlated methods; in these calculations the configuration state functions contain an explicit correlating factor

$$F = \exp\left(-\beta r_{12}\right) \tag{4}$$

For all explicitly correlated calculations for valence correlation energies, we have used β = 0.9 a. u. for the jul-D basis set and β = 1.0 a. u. for jul-T basis set, based on recommendations by Peterson et al.[9] and Hill et al.[19] The default value for β in *Molpro* is 1.0. The supporting information gives input examples for setting β to the nondefault values of the WMS calculations.

In all of the explicitly correlated coupled cluster calculations, we have employed the fixed-amplitude 3C(FIX) ansatz[20-22] for the CCSD(T)-F12b method of Knizia et al.[22,23] The 3C(FIX) ansatz is the default in *Molpro* ; the F12b method is expected to slightly underestimate the full F12 energy.

4.2.4 CCSD Valence Correlation Energy. In the WMS model, the CCSD-F12 correlation energy (which equals the CCSD energy minus the HF energy) is decomposed into three contributions:

$$\mathrm{E(CCSD\text{-}cor) = E(MP2\text{-}cor) + E(F12) + E(CCSD\text{-}HO)} \qquad (5)$$

where

$$E(\mathrm{MP2\text{-}cor}) = E(\mathrm{MP2}) - E(\mathrm{HF}) \qquad (6)$$

$$E(\mathrm{F12}) = E(\mathrm{MP2\text{-}F12}) - E(\mathrm{MP2}) \qquad (7)$$

and

$$E(\mathrm{CCSD\text{-}HO}) = E(\mathrm{CCSD\text{-}F12}) - E(\mathrm{MP2\text{-}F12}) \qquad (8)$$

4.2.5 The Scalar Relativistic Component. The scalar relativistic contribution (in the second-order Douglas–Kroll–Hess approximation)[24,25] is extrapolated as the difference between non-relativistic MP2/jul-*n* (where (*n* = D or T) and relativistic MP2/jul-*n*-DK calculations using Eq. (3) with α = 2.0.

4.2.6 The Core-Valence Correlation Component. The calculation of the core-valence correlation component can be a bottleneck of the computational cost of a composite method because of the demanding full-electron correlation calculations. We employed separate extrapolation of the MP2 and CCSD-minus-MP2 contributions to obtain the CCSD core-valence correlation. The total core-valence correlation contribution for WMS is defined as:

$$\Delta \mathrm{E}_{\mathrm{CV}}^{\mathrm{WMS}} = \Delta \mathrm{E}_{\mathrm{MP2}}^{\mathrm{CV-CBS}} + (\Delta \mathrm{E}_{\mathrm{CCSD}}^{\mathrm{CV}} - \Delta \mathrm{E}_{\mathrm{MP2}}^{\mathrm{CV}} + c\Delta \mathrm{E}_{\mathrm{(T)}}^{\mathrm{CV}})_{\mathrm{wCVD}} \qquad (8)$$

where $\Delta E_{\mathrm{MP2}}^{\mathrm{CV-CBS}}$ is extrapolated with the wCV{D,T} basis sets using Eq. (3) and the optimized α is 3.55. The perturbative triple excitation contribution of Eq. (8) is evaluated with the wCVD basis set, and scaled by an optimized factor *c* = 3.8. As described in Section 4, the parameter α and c for the CV calculations are optimized globally (along with the parameters in valence correlations) against the TAEs of W4-17.

We tried using the CCSD(T)-F12b method to calculate the core-valence correlation, but we found that it is inferior to CCSD(T) from the standpoint of cost-to-performance. We also found that the wCVD basis set gives better performance than the CVD basis sets when combined with CCSD(T).

4.2.7 Spin-Orbit Coupling. To first order, E_{SO} is zero by symmetry for closed-shell molecules, for linear molecules in Σ states, and for singlet and doublet molecules in A or B states. For cases with nonzero E_{SO}, it can be obtained from experiment for monatomic species (from data in Moore's tables,[26] which are reproduced, with only slight updates, on the NIST website) and by calculations for molecules (e.g., by state-averaged complete active space self-consistent field calculations).

In the present study, E_{SO} values for calculating atomization energies have been taken from the W4-17 paper.[27] (they could also be computed on the back of an envelope for any monatomic species by using Moore's tables). For DBH24, the nonzero E_{SO}values for F, Cl, and OH are taken from a previous paper,[28] and E_{SO} for SH is taken from our BMC-CCSD paper.[29] For the reactions of Criegee intermediates, all the E_{SO}values are zero.

4.2.8 Optimized parameters. The optimized parameters for the WMS valence correlation energies are in Table 4. All parameters are positive and greater than unity, as expected for a physical extrapolation.

Table 4. Optimized parameters for WMS

Coefficients	Value
c_{HF}	2.178
c_{CABS}	2.309
c_{MP2}	1.018
c_{F12}	1.126
c_{CCSD}	1.569
$c_{(T)}$	2.175

4.3 Definition of the W2X, W3X, and W3X-L Methods

The components of the W2X, W3X, and W3X-L Methods are defined in Table 4.

Table 4. Definition of the W2X, W3X, and W3X-L methods

Components	**W3X-L**	**W2X**	**W3X**
$\Delta E_{\mathrm{HF}}^{\mathrm{CBS}}$	HF*/jul-VQ	Same as W3X-L	extrapolation of HF* using V{D,T}Z-F12
$\Delta E_{\mathrm{CCSD}}^{\mathrm{CBS}}$	extrapolation of CCSD using jul-V{T,Q} with an α of 5.88	Same as W3X-L	CCSD-F12b/ V{D,T}Z-F12
$\Delta E_{\mathrm{(T)}}^{\mathrm{CBS}}$	1.06*$E_{(T)}$ using jul-VT	Same as W3X-L	(T)/jul-V{DT}
$\Delta E_{\mathrm{CV}}^{\mathrm{CBS}}$ + $\Delta E_{\mathrm{Rel}}^{\mathrm{CBS}}$	The CV and scalar-relativistic components are calculated together using a composite approach: 1.14 E[MP2]/CVT(3d) + 1.56E[ΔCCSD(T)]/CVD(2d)	Same as W3X-L	MP2/CVTZ
$\Delta E_{\mathrm{HOVC}}^{\mathrm{CBS}}$	E[CCSDT − CCSD(T)] extrapolated with VD(NP) and VT(d) (α = 2.61) plus 0.78E[CCSDT(Q)-CCSDT]/VD(d)	N.A.	1.14E[CCSDT − CCSD(T)] /VT(NP) +0.69E[CCSDT(Q)-CCSDT]/VD(NP)
ΔE_{SO}	Experiment	Experiment	Experiment

Chapter Five

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5. Input Description

There are ten *Perl* scripts in *WMPack* , and they use different types of geometric input file.

mWMS.pl is a script for preparing the *Molpro* input files for the WMS method. It takes a geometry input file of the xyz format, and generate a *Molpro* input file with an extension .com. The example xyz input for H_2O is as follows:

h2o.xyz

```
3
0  1
O  0.000000  0.000000  0.117790
H  0.000000  0.755453  -0.471161
H  0.000000  -0.755453  -0.471161
```

The first line in h2o.xyz is the number of atoms in the molecule, and the second line is for the charge and spin multiplicity of the molecule. The Cartesian coordinate of each atom starts from the third line.

If one issues the following command:

```
perl mWMS.pl h2o.xyz
```

A file named h2o_WMS.com will be generated by the mWMS.pl script.

The user can invoke the *Molpro* program to do the WMS calculations, for example

```
molpro –n 4 h2o.com
```

After the *Molpro* calculation is done, the *Molpro* program will generate the h2o.out output file.

One can extract the WMS energies by using the rWMS.pl script:

perl rWMS.pl h2o.out

The geometry input file for the mWMS_gs.pl, mW3XL_gs.pl, and mW2X_gs.pl scripts is a *Gaussian* single-point energy output file.

The geometry input file for the mWMS_go.pl script is a *Gaussian* geometry optimization output file.

The geometry input file for the mWMS_mo.pl, mW3XL_mo.pl, and mW2X_mo.pl scripts is a *Molpro* geometry optimization output file.

Chapter Six

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6. Installing and using *WMPack*

The *WMPack* program needs the *Molpro* and *MRCC* software programs as the computing engines, and the installation of *Molpro* and *MRCC* should follow their documentation.

The *WMPack* program should have been obtained in the tar format with the following file name: *WMPack* 1.0.tar.gz. This file should be placed in the directory in which the user wishes to install *WMPack*, and then the following two commands should be executed:

```
ungzip WMPack1.0.tar.gz
tar –xvf WMPack1.0.tar
```

Verify that the files have been placed into the directory structure as follows.

In the *WMPack1.0* directory:

documents/
script/
testi/
/testo

In the *documents* directory:

WMPack_Manual_v1.0.pdf

In the *script* directory:

mW2X_gs.pl
mW2X_mo.pl
mW3X_gs.pl
mW3XL_gs.pl
mW3XL_mo.pl
mWMS_go.pl
mWMS_gs.pl
mWMS_mo.pl
mWMS.pl
rWMS.pl

In the *testi* directory:

ch3.xyz
h2o.xyz
h2s.out
Li2S3.out
vinylperoxy.out

In the *testo* directory:

ch3_WMS.com
h2o_WMS.com
h2s_W2X.com
h2s_W3X.com
h2s_W3XL.com
h2s_WMS.com
Li2S3_W2X.com
Li2S3_W3XL.com
Li2S3_WMS.com
vinylperoxy_WMS.com

The *WMPack* program should have been installed correctly in your home directory. The user can test the installation by using the test input files in the *testi* directory. To do this, change the working directory to the *testi* directory and execute the following commands:

```
perl ../script/mWMS.pl ch3.xyz
perl ../script/mWMS.pl h2o.xyz
perl ../script/mWMS_gs.pl h2s.out
perl ../script/mWMS_go.pl vinylperoxy.out
```

```
perl ../script/mWMS_mo.pl Li2S3.out
perl ../script/mW3X_gs.pl h2s.out
perl ../script/mW3XL_gs.pl h2s.out
perl ../script/mW2X_gs.pl h2s.out
perl ../script/mW3XL_mo.pl Li2S3.out
perl ../script/mW2X_mo.pl Li2S3.out
```

After the executions, ten *Molpro* input files should have been generated, and the user can use the *diff* command to compare the newly generated files to those in the *testo* directory. Note that all of the mWxxxx.pl scripts can take multiple geometry input files. For example, the user can use the following command to generate two or more WMS, W2X, W3X, or W3X-L input files:

```
perl ../script/mWMS ch3.xyz h2o.xyz
perl ../script/mW3XL_mo.pl *.out
```

The user can invoke the *Molpro* program to do the WMS calculations, for example

```
molpro –n 4 h2o.com
```

After the *Molpro* calculation is done, the *Molpro* program generates an output file, h2o.out. One can extract the WMS energies by using the rWMS.pl script:

```
perl rWMS.pl  h2o.out
```

The W2X, W3X, and W3X-L energies are self-contained in the *Molpro* output files.

Chapter Seven

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7. Computers, Operating Systems, and Software Tested

In each case we give the *WMPack* version number and the computers and operating systems on which *WMPack* was tested. For each computer, we also specify the operating system.

WMPack 1.0

Computer	Operating System	Software
INSPUR Cluster	CentOS Linux release 7.2.1511	*Molpro* 2015, MRCC(2017-09-25 binary), and *Gaussian 09* D01
Wuzhou Cluster	CentOS Linux release 7.4.1708	*Molpro* 2015, MRCC(2017-09-25 binary), and *Gaussian 09* D01
MSI Mesabi Cluster	CentOS Linux release 7.5.1804	*Molpro* 2015, MRCC(2017-09-25 binary), and *Gaussian 09* D01

Chapter Eight

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8. Bibliography

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Chapter Nine

9

9. Revision History

9.1 Version 1.0

Authors of this version: Y. Zhao and D. G. Truhlar.

First distributed version

End of Manual