ADANIMEHS

(ADaptive ANalysis of InterMolecular Energy HyperSurfaces)

Software User Manual

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Nizhny Novgorod 1999-2007

1. INTRODUCTION

Adanimehs is a program for efficient quantum chemical exploration of potential energy surfaces (PES) of structurally non-rigid molecular complexes, approximation or interpolation of PES with a model continuous function, and estimation of thermodynamic parameters of the complex using the classical Monte-Carlo calculations.

In comparison with other tools, Adanimehs has two crucial advantages:

- *Ab initio* exploration of full (multidimensional) intermolecular PES instead of location of selected stationary points only.

- Calculation of thermodynamic properties in the approximation higher than the usually employed rigid rotor –harmonic oscillator (RRHO) model. It allows obtaining the high-accurate values of equilibrium constants and concentrations for weakly bound systems like van-der-Waals and H-bonded complexes or clusters.

2. COMMON RULES FOR THE COMPILATION OF INPUT FILES

Structure of Input files (*.gsd):

```
<Beginning of file>
PHASE1
Command1 for phase1
Command2 for phase1
…
PHASE2
Command1 for phase2
Command2 for phase2
…
PHASE3
Command1 for phase3
Command2 for phase3
…
PHASE4
Command1 for phase4
Command2 for phase4
…

<End-of file>
```

The common rules for the input file:

1. The small and capital letters are not distinguished.
2. Blank lines are not considered except the cases when the blank line is a command terminator.
3. All the lines can be marked with comment sign “!” in the first position except of cases indicated specially. These lines are comments which are not used in the calculations.

PHASE keywords designates the beginning of new phase of work (new part of calculations). Phase description:

PHASE1 **-** Description of molecular fragments, scanning procedure and job options

PHASE2 **-** Description of QC run, post-QC calculations, restart and import options

PHASE3 **-** Options for potential approximation (interpolation)

PHASE4 - Options for thermodynamic calculations

3. THE COMMAND DESCRIPTIONS FOR THE CORRESPONDING PHASES

PHASE1

Fragment *fragment name*	Start molecular fragment named *fragment name*
atom X Y Z	Atom symbol and cartesian coordinates
…	…
…	…
blank line	Finish fragment with blank line

Centered	set center of mass of fragment to the coordinate origin
Oriented	**s**et center of mass of fragment to the coordinate origin and reduce it to the principal axes
Translate *x y z*	translate fragment by vector *x y z*
RotateX *angle*	rotate fragment by *angle* around OX axes
RotateY *angle*	rotate fragment by *angle* around OY axes
RotateZ *angle*	rotate fragment by *angle* around OZ axes

ScanProc Start scanning procedure description (blank line – finish)

[**RotateX** *FragmentName* *BegVal* *EndVal* *Delta* [*SymCond*]]
[**RotateY** *FragmentName* *BegVal* *EndVal* *Delta* [*SymCond*]]
[**RotateZ** *FragmentName* *BegVal* *EndVal* *Delta* [*SymCond*]]
[**RotateA** *FragmentName* *BegVal* *EndVal* *Delta* [*SymCond*]]
[**RotateB** *FragmentName* *BegVal* *EndVal* *Delta* [*SymCond*]]
[**RotateC** *FragmentName* *BegVal* *EndVal* *Delta* [*SymCond*]]
[**RotateG** *FragmentName* *BegVal* *EndVal* *Delta* [*SymCond*]]
[**RotateBond** *FragmentName* *BegVal* *EndVal* *Delta* [*SymCond*]]
[**TranslateX** *FragmentName* *BegVal* *EndVal* *Delta* [*SymCond*]]
[**TranslateY** *FragmentName* *BegVal* *EndVal* *Delta* [*SymCond*]]
[**TranslateZ** *FragmentName* *BegVal* *EndVal* *Delta* [*SymCond*]]
blank line

FragmentName	- Name of fragment (as given in **Fragment** keyword)
BegVal	- Initial value of scanning coordinate
EndVal	- Final value of scanning coordinate
Delta	- Increment of scanning coordinate Thus, the number of points in the current direction of PES is: *N*=[(*EndVal*-*BegVal*)/*Delta*]
SymCond	- Symmetry condition on low and upper boundaries (on LB and UB). *SymCond*:= **AA|SA|AS|SS|C-|C+**

AA – LB and UB are asymmetric (no relations between *F*(LB) and *F*(UB)) (*Default*).
AS – LB asymmetric, UB symmetric: *F*(UB+1)=*F*(UB-1)
SA – LB symmetric, UB asymmetric: *F*(LB-1)=*F*(LB+1).
SS – LB and UB are symmetric: *F*(LB-1)=*F*(LB+1), *F*(UB+1)=*F*(UB-1)
C– – LB and UB are cyclic: *F*(LB-1)=*F*(UB), *F*(UB+1)=*F*(LB)
C+ – LB and UB are redundantly cyclic: *F*(LB)=*F*(UB), *F*(LB-1)=*F*(UB-1), *F*(UB+1)=*F*(LB+1)

Here, *F*(LB) is a value of the PES function on LB (at the first point of the given DPES coordinate), and *F*(UB) – on UB (at the last point of the current DPES coordinate)

PrintFullTable - print full table of scanned points (instead of unique points only which is a default print mode)

Export *filename[.exp]* - export the calculated table (condensed) to the external file

ExportFullTable *filename[.exp]* - export of full table to the external file

PrintGeo **-** print the cartesian coordinates of scanned points

PrintLevel *Level* - set level of printing: *Level* = **0** () **|** **1** ()

List Point|Uniq|Index [**Recalc**] [**NoGeo**] [**Surround**] - print the selected point(s) from the table
point number | unique point number | indexes
…
blank line

Options: **Point –** set points by global numbers
Uniq - set points by unique numbers
Index - set points by indexes
Recalc – recalculate points before printing
NoGeo – don't print Cartesian coordinates of points
Surround – print point(s) together with all the neighboring points

Example:
List Uniq Surround
1234
4256
12387

Plot [*inactive coord values*] **X** [*inactive coord values*] [**Y**] [*inactive coord values*]

- print the section of table in the form suitable for 2D or 3D plotting
- *inactive coord values* –values of fixed coordinates
- **X|Y –** marks the coordinates which should be plotted as X or Y values

Example:
Plot 0 0 0 X Y 60

Index [**Calc** <Method> [<NmaxPoint>] | **Read** <filename.ext>] -

- Method for determination of unique point indexes:

Calc – calculate indexes.

<Method>:

1 – Search of equivalent structures, then testing of selected points on the basis of quasi-energy values (most reliable but time-consuming method).

2 – Testing of quasi-energies without the preliminary structure comparison. <NmaxPoint> is required for this option: max number of unique points. Default: NmaxPoint=number of all points. However, the default value can result in memory lack. In this case, set NmaxPoint to a lesser value.

3 – Testing of quasi energies presented as integer vector (obsolescent option, not reliable)

Read – import indexes from the file <filename.ext> prepared during previous run for the considered system. After each successful calculation of indexes, Adanimehs creates the index file <input_file_name.ind> which can be used during the next runs to save time for index calculations. This file can be used without any changes. Default for <filename.ext> = <input_file_name.ind>

Default for Index command: **Index Calc 1**.

Example:

Index Calc 2 30000
Index Read (H2O)2.ind

NoEqual **-** don't determine the unique points (make all the calculations on the basis of the full PES table). This is obsolescent option. Some further calculations do not support this mode.

ErrPoints [**<u>Interpolate</u>** <iDim>| **Ignore** <ErrFVal> | **Stop** | **List** | **Find** <ErrFVal>]

- Actions to be undertaken when a non-fatal error is occurred during the energy calculation at the current grid point. Usually this means that the program could not find the energy pattern in the output file of the QC program (probably because SCF was not converged or another error was happened during the energy calculation). In this case the energy of the point is set to 999999 and the point is marked as erroneous one with mark (E). Adanimehs can correct these values in the next runs using the commands:

Interpolate – define the unknown value by the cubic interpolation from the known points in the preferable dimension iDim of the calculated grid. If the interpolation impossible, another dimension will be chosen automatically. This is a default action. Default iDim=1.

Ignore – set energy values of error points to ErrFVal and continue calculation. (Default ErrFVal=999999.)

Stop – stop after the grid calculation if the error points are occurred.

List – Print out the list of erroneous points and their coordinates.

Find – find the points with E = <ErrFVal> and mark them as error points. Default ErrFVal=999999. This option is useful during importing and extracting the points from external file.

Exit **-** finalize the job after current PHASE

PHASE2

JobFile <file name>	- sets the input file name of QC program (Default: *scan.inp*)
ResFile <file name>	- sets the output file name of QC program (Default: *scan.out*)
PunFile <filename>	- sets the auxiliary data file name of QC program (reserved for further development)
RunCommand <run command>	- command string to start the QC program
JobPattern	- QC program commands describing the method of calculation and the necessary job options in the QC program input file. It should contain the proper keywords of the corresponding QC program combined with expressions like %FragName1%, %FragName2%, etc. indicated at the place when the geometry of fragments should be located. If it is required the comment can be inserted by expression %Comment%. The blank lines can be inserted as well. The Job Pattern should be terminated by **EndJobPattern** keyword. Fragment name(s) should completely correspond to the names assigned in PHASE1. Thus, the complete JobPatter should be looked like this:

JobPattern
<keywords of QC program>
%Comment%
<other keywords>
%*fragment name***%**
[**%***fragment name***%**]
<more keywords if needed>
EndJobPattern

Example of the JobPattern command to organize the PC GAMESS energy calculations in the PES points:

```
JobPattern
 $CONTRL MAXIT=200 SCFTYP=RHF RUNTYP=ENERGY
MPLEVL=2  $END
 $SYSTEM TIMLIM=30000 MEMORY=12000000 $END
 $SCF DIRSCF=.TRUE. $END
 $BASIS GBASIS=N311 NGAUSS=6 NDFUNC=2 NPFUNC=2
   DIFFSP=.TRUE. DIFFS=.TRUE. $END
 $DATA
SO2- -H2O (Monomer geo - MP2/6-311++G(2d,2p) optimized)
C1
```

```
%SO2%
%H2O%
 $END
EndJobPattern
```

ResultPattern
<result pattern> - pattern to find the string in the QC-program output file containing the necessary data. The value should be found at the same line and be separated by spaces from the end of result pattern and the next word of the line. I.e. result pattern “MP2 energy =” allows extract the MP2 energy from the file containing the string:
“MP2 energy = -123.456789 a.u.”.

BSSE *number* - perform BSSE calculations *(under development)*

GuessPunch **-** use initial guess from the previous file *(under development)*

PostCommand **-** perform additional arithmetic calculations on the calculated energies
post command1
post command2
...
blank line

Example:

%2 = %1 40.3943219177 + 76.2988008439 + (calculate 2-nd column of energy table by addition of energies of two fragments to the 1-st column)

%3 = %2 27.21 * 23.06 * (convert energy from a.u. (in 2-nd column of Table) to kcal/mol and place it to 3-rd column)

Analyze *ColumnNumber* - use the energy from the corresponding table column for further analysis (finding minima, interpolation etc.)

Restart *filename.ext* - restart calculations using the output file *filename.ext* from previous (not finished) run or from the file with the same S**canProc**

Import *filename.ext*
current indexes
imported indexes
-import part of table from the external file (probably with other **ScanProc**)

Extract *IUPfile.ext GSOfile.ext* - extract data from the file *GSOfile.ext* of previous run using the IUP keys of previous run taken from *IUPfile.ext. Warning! IND file and IUP file of the current run should be present or calculated.*

AutoImport <filename>	-import part of table from the external file using the geometry coordinates only (probably with other **ScanProc**). The point will be imported if its geometry corresponds to the geometry of any point in the current Table
NOQC	- do not perform the QC calculations
NoLMAnalysis	- do not perform the search for minimum points on discrete PES
LInterPlot <*np***>** *<Xbeg>* *<Xend>*	- print the table of *np* interpolated energy values at points: *X=Xbeg+(i-1)*(Xend-Xbeg)/(np-1), i=1,2,3…np* *Xbeg* and *Xend* are vectors of *N* values (*N* is PES dimension) This is useful for drawing of 1D-plot of interpolated values in the arbitrary PES points (points not coincided with nodes). Example: LInterPlot 21 0. 47. 23. 2.0 180. 91. 0. 34. 358. 4.0 180. 91.
LInterPlot *<np> <mp>* *<Xbeg>* *<Xend>* *<Yend>*	- print the interpolated energy values at points (2D plot): *X=Xbeg+(i-1)*(Xend-Xbeg)/(np-1)+(j-1)*(Yend-Xbeg)/(mp-1),* *i=1,2,3…np; j=1,2,3…mp*

PHASE3

Optimization <Method> <MaxFcn> <Tol> - method for potential function fitting:

<Method> :

[0] – Don't optimize potential (do single calculation of the approximate PES using the user-provided parameters)

1 – Quasi-Newton BFGS-based (Powell, 1988) optimization with simple bounds and linear constraints (numerical calculation of gradients)

2 – Simplex optimization with simple bounds (gradientless)

3 – Simplex optimization without constraints (gradientless)

4 – Quasi-Newton optimization without constraints (numerical gradients)/

<MaxFcn>: Maximum number of function evaluation

<Tol> : Accuracy goal

5 – Perform Monte-Carlo search in a coordinate space and select 10 points with lowest value of discrepancy. This can be used as a preliminary search of the starting point for further optimization. Number of points in the Monte-Carlo search is MaxFcn*100. Default value = 100000.

Weighting <Type> <w_0> <T_w> - type of weighting of point energy during the potential fitting:
<Type>:
0 – no weighting: all points are equivalent (weighting factor $w_i = 1$ for all points i).
1 – exponential weighing with "temperature" <T_w>. The points will be weighted with factor $w = w_0 * \mathrm{Exp}(-E_\mathrm{i}-E_\mathrm{min})/RT_\mathrm{w})$, where E_i – exact energy of the point i, E_min – energy of global minimum on a discrete grid, R =8.314 J/K/mol – gas constant, T_w – "weighting temperature", K, w_0 – a constant factor. This is a default weighting with defaults: w_0=1, T_w=298.15.
2 – stratified weighting (rarely used).

ELimit <Elim> - during optimization, take into account only the points with energy lower Elim (Set weighting factor to 0 if the energy is higher than Elim). Default Elim=99999 kJ/mol. Thus, the error points (E=999999) will not be taken into account by default.

NoLMOpt - do not optimize structure of local minima after the potential fitting. By default, the local minima will be optimized and their frequencies will be calculated.

Potential description:

<Potential Type>
<Center1 description>
…
<CenterN description>
blank line
<Parameter1 value>
…
<ParameterN value>

<Potential type> specifies that the type of potential function is presented in the model potential. It can be of four types:
Multipole
Exchange
Dispersion
Induction

<Center description> :: =
<Parameter name> <Type> <OptFlag> <FragmentNo> <Center type> <N1> [[N2] [N3]]

<Parameter Name>	name of the given parameter of the potential , e.g. qH for charge of atom H, alpO for polarizability of atom O etc.
<Type>	- type of parameter: **0**, **1**, **2**, **3**. Each kind of potential terms have the corresponding types. E.g. Multipole Type can be **0** (charge), **1** (dipole), **2** (quadrupole) etc. Exchange Type can be **0** (*a* value), **1** (*b* value), or **2** (pair of *a* and *b*) in a potential term *u*=*a**Exp(-*b***R*). Dispersion and Induction types should be **1.**
<OptFlag>	- If <OptFlag>= ***** , the parameter will be adjusted during the parameter optimization. If the parameter should be fixed, use any other symbol.
<FragmentNo>	- Fragment number where the center is located. If 0, the center is located in the whole molecule. If >0, it will be located only in the given fragment
<Center Type>	Place where the center should be located: **A** – atom number N1 in a fragment <FragmentNo> **B** – bond between atoms N1 and N2 **C** – center of mass of fragment <FragmentNo> **P** – arbitrary point with coordinates (N1, N2, N3) **E** – all elements with atom number N1

<Parameter Value>::=
<Parameter Name> <Val1> [Val2> [Val3]…]] [<LB1> [<LB2>…]] [<UB1> [<UB2>…]]
<Parameter Name> should correspond to the name given in <Center description>.

<Val1>	value of the given parameter
<Val2>, <Val3>, …	second and other values of the parameter (it is required for some types of parameters) E.g. for "Multipole Type 1" (dipole moment) three values are required: Dx, Dy, Dz. Two values (*a* and *b*) are required for "Exchange Type 2" : *u* = *a**Exp(-*b***R*))
<LB1>, <LB2>…	Lower boundaries for the parameter during the optimization
<UB1>, <UB2>…	Upper boundaries for the parameter during the optimization

---

PHASE4

Keywords for thermodynamic calculations:

Temperature [C] <*T1*> [<*T2*> <T3>…] - temperatures or temperature ranges for TD calculation. Each <*Tn*> parameter can be either a single temperature or the temperature range of type **(***Tbeg***:***Tend*/*StepT***)**. In the last case, the TD calculations will be performed for each temperature T_i defined by expression $T_i = Tbeg + i*StepT$, i = 0,1,2…INT[(*Tend-Tbeg*)/*StepT*]

Example:
Temp 298.15 373 (200:400/50)
This example means that the TD functions will be calculated for the temperatures: 298.15, 373, 200, 250, 300, 350, 400 Kelvins.
Default value (used if Temp is not set): T=298.15 K
Temperatures in degrees of Celsium can be requested in Temp instead of Kelvins by indication of **C** option after Temp keywords:
Temp C 100 250 300

Pressure <*P*> <Units> [<*Pend*><*StepP*>] - pressure range for TD calculations
P – initial temperature. Default: *P*=101325 Pa.
Units – pressure units: **atm**, **Pa**, **bar**
Pend, StepP – final pressure and pressure step. If set, the TD calculations will be performed for each pressures
$P_i = P + i*StepP$, i = 0,1,2…INT[($Pend$-P)/$StepP$]

Multiplicity <Frag0> <Frag1> <Frag2> … - Multiplicity of complex and monomers.
Defaults: 1 for all the fragments.

Edis <D_e | **GME** | **GMA** | **GM**| **ET**OT> <Units> - Dissociation energy D_e in Units: kJ/mol **kJ ,** kcal/mol **kcal,** electron-volts **eV,** Hartees **au.**
GME – determines D_e from Global Minimum on exact (discrete) PES
GMA – determines D_e from GM on approximate PES
GM – determines D_e as Min(GMA,GME)
ETOT – determines D_e as D_e = Etot(Complex AB)-Etot(A)-Etot(B).
Etot should be provided for complex and monomers (see below).

Distance <*R*> - equilibrium distance between monomers in complex (Angstroems). It is used to set the initial moment of inertia. It is rarely needed, usually determined automatically from the GM structure.

Etot <FragNo> <E> [<Ea> <Eb> <Ec> <Ed>] - Total energy for fragment Frag (0,1,2,….) in Hartrees. If FragNo=0 and Ea, Eb, Ec, Ed are provided, the BSSE is automatically calculated. In the last case:
Ea – total energy of (monomer 1 + ghost atoms of monomer 2)
Eb – total energy of (monomer 2 + ghost atoms of monomer 1)
Ec – total energy of (monomer 1 in the geometry of complex)
Ed – total energy of (monomer 2 in the geometry of complex)

BSSE <BSSE> <Units> - BSSE value which should be used to correct D_e. Units: kJ/mol **kJ**, kcal/mol **kcal**, electron-volts **eV**, Hartrees **au.**

EModel <Type> - model for the potential energy calculations. Type:
1 – interpolation of the DPES values by linear polynomials (default)
2 – approximation of the potential energy using the model potential described (and probably parameterized) at PHASE 3

KinTyp <Type> - method of kinetic energy calculation. Type:
1 – approximate (faster) calculation using the approximate formulas

2 – exact (slower) calculation using the exact expression of T

MCtyp <Type> <Npoints> - method of Monte-Carlo calculations. Type:
1 – MCC with flexible boundaries (fast) (Default Npoints=10000)
2 – MCC with fixed boundaries (Default Npoints=100000)
Npoints – number of MCC points.

Eintegration <Emax> <dE> - upper integration limit (Emax) and step (dE) for energy during Z calculation. They should be set in kJ/mol. Defaults: Emax=50, dE=0.5.

Rintegration <Rmin> <Rmax> - integration limits in W(E) calculations (in Angstroems). Defaults: Rmin=…, Rmax=…

Correction <Type> <CorrFactor> - type of quantum correction of statistical integral
Type:
0 – no correction,
1 - quantum correction with CorrFactor= Z(H.O.quant)/Z(H.O.classic),
2 – correction using the provided correction factor

RefGeo <FragNo> <Format> - Read the reference geometry for fragment FragNo and use it in the TD calculations instead of initial geo used during the PES scan. The next N lines should contain the atom description and coordinates in Format: **1** – NXYZ, **2** - NDXYZ, **3**- DNXYZ. The geometry should be terminated with blank line.

Frequencies <FragNo> <ScaleFactor>
<freq> [<mode descriptor> <degeneracy>]

Freq: - frequency in cm^{-1}
Mode descriptor:
– - do not use the mode in TD calculation
0 - zero mode (translation or rotation of molecule as whole)
H – harmonic mode (include it as harmonic contribution)
A – anharmonic mode
I – internal rotation
X – active (rovibrational) mode
Degeneracy: mode degeneration (default: 1)

4. ADANIMEHS DISTRIBUTION AND UPDATES

ADANIMEHS is distributed as a free executable. The only requirement for its use is an appropriate referencing if you publish the results obtained with it (e.g. results of TD calculations). Please refer the program version you used as follows:

S.K.Ignatov, Adanimehs v.1.0, http://ichem.unn.ru/Adanimehs, 2007.

PLEASE NOTE THAT ADANIMEHS IS A RESEARCH SOFTWARE AND DISTRIBUTED ON "AS IS" BASIS. WE SHOULD APPRECIATE RECEIVING YOUR COMMENTS, ADVICES, BUG REPORTS AND REQUESTS FOR FURTHER IMPROVEMENTS.

The newer versions of ADANIMEHS and documentation can also be found at
http://ichem.unn.ru/Adanimehs

5. ADDRESSES

Please send your comments, questions, advices, bug reports, and requests for further improvements to:

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