

GAMESS-UJ documentation

Peilin Liao, Nicholas J. Mosey, Emily A. Carter

I. Introduction

We have developed two methods for calculating U and J from unrestricted Hartree-Fock calculations. Our initial effort is described in Phys. Rev. B 76, 155123 (2007), followed by a rotationally-invariant formalism described in J. Chem. Phys. 129, 014103 (2008). "GAMESS-UJ" refers to the second method implemented in the GAMESS package (<http://www.msg.ameslab.gov/games/>).

II. Programmer's guide

a. How to obtain the code

The *ab initio* evaluation of U and J is implemented in GAMESS (GAMESS VERSION = 22 FEB 2006 (R5)). Five source files were modified. We provide these five modified files.

Interested users may request the 2006 GAMESS code from Dr. Mike Schmidt (mike@si.msg.chem.iastate.edu), or download the latest version of GAMESS and make intelligent changes at the relevant places in those files.

b. Changes made to the source files

A few subroutines were modified to get GAMESS to calculate U and J . The basic information of these modifications is given below. Detailed modifications are commented in the source files. All modifications made to the code are bracketed with CMOSEY. That is, if you go into any subroutine you can search for 'CMOSEY' and you should find something like:

```
...  
Unmodified code
```

```
...  
CMOSEY  
Modified code  
CMOSEY
```

```
...  
Unmodified code
```

```
...
```

The following GAMESS source files are modified:

games.src

- Control the progress of the program
- Modification: avoid redundant printing

prppop.src

- Perform population analysis
- Modification: added a small block to calculate the populations of each atomic basis function in each molecular orbital using the existing Mulliken population analysis in GAMESS

int2a.src

- Calculate the two-electron integrals in the basis of the atomic orbitals

- Modification: set up a progress counter

rhfuhf.src

- Performs the UHF calculation
- Modified extensively to calculate U and J : check if U and J calculation is requested; get the alpha and beta molecular orbital coefficients from the converged UHF wavefunction; calculate U and J

scflib.src

- Build the Fock matrix with direct SCF methods
- Modification: calculate Coulomb and exchange energies with the alpha/beta density matrix in the atomic orbital basis using Fock matrix techniques; calculate the self-interaction energy in the molecular orbital basis

III. User's guide

a. Overview of how the code works

The method for calculating U and J uses unrestricted Hartree-Fock calculations of a small cluster embedded in effective core potentials and point charges. The steps involved in the calculation of U and J are:

1. Install the modified version of GAMESS
2. Set up embedded cluster calculations
3. Solve for the appropriate electronic structure
4. Evaluate U and J after the wavefunction has converged

b. Compile GAMESS-UJ

For compiling the unmodified GAMESS, please refer to the GAMESS manual (available on the GAMESS website) for details. Please make sure you have a working version of GAMESS before compiling GAMESS-UJ.

Step 1. Extract the files by:

```
tar -xvzf gamess-uj.tgz
```

The *gamess-uj/src_modified* folder contains the modified source files, and the *gamess-uj/test* folder contains input and output files for three test cases.

Step 2. Use the five sources files provided to replace the corresponding ones in the *gamess/source* directory. Recompile the code. Modify the *gamess/rungms* script to copy OrbsAA file to the scratch directory during initialization.

Step 3. Run the three test cases provided. Make sure the U - J values match the ones in the corresponding output files.

c. Computing U and J

The following describes how to calculate U and J with GAMESS-UJ. It is assumed that you already have a GAMESS input file set up and have been able to converge the electronic structure to the appropriate state.

Step 1. Set up the OrbsAA File

In the directory where you will run GAMESS-UJ, put the input file that gives you a converged electronic

structure. In the same directory, make a file called OrbsAA. The presence of this file tells GAMESS to calculate U and J .

The first line in the OrbsAA file specifies the numbers of the first and last d-type basis functions on the atom for which you want to calculate U and J . These basis functions are used to get the orbital populations.

The second line in the OrbsAA file provides a population threshold for determining which self-interaction integrals are calculated. Basically, if the number of localized d electrons in a molecular orbital is below this threshold, the associated self-interaction integral is not calculated. Experience with chromia shows that a threshold of 5.0e-3 removes 90% of the self-interaction integrals for large systems, and only affects U-J by 0.01 eV. You should check this for your system, however.

An example OrbsAA file is:

```
13 24
0
```

The specific limits of 13 and 24 will tell GAMESS-UJ to use all of the basis functions between number 13 and 24 (inclusive) to calculate the orbital populations used to get U and J . You can figure out the basis function numbers by looking for the 'EIGENVECTORS' section of the GAMESS output and seeing which basis function numbers correspond to d-type basis functions on the atom of interest. For instance, if you were interested in calculated U and J for atom 1 of the system in *test/fe2o10/hem2.inp* that yielded the following 'EIGENVECTOR' section, you would put the limits at 13 and 24, as those numbers correspond to the start and end of the d-type basis functions on atom 1.

...

13	FE 1 XX	-0.000040	0.000154	0.000000	0.000000	-0.000072
14	FE 1 YY	-0.000040	-0.000154	0.000000	0.000000	-0.000072
15	FE 1 ZZ	0.000081	0.000000	0.000000	0.000000	0.000144
16	FE 1 XY	-0.000016	0.000000	0.000000	0.000000	-0.000006
17	FE 1 XZ	0.000000	0.000000	0.000007	-0.000015	0.000000
18	FE 1 YZ	0.000000	0.000000	-0.000007	0.000015	0.000000
19	FE 1 XX	0.000427	-0.001487	0.000000	-0.000001	0.000687
20	FE 1 YY	0.000427	0.001487	0.000000	-0.000001	0.000687
21	FE 1 ZZ	-0.000855	0.000000	0.000000	0.000001	-0.001374
22	FE 1 XY	0.000104	0.000000	0.000000	0.000000	0.000048
23	FE 1 XZ	0.000000	0.000000	-0.000055	0.000083	0.000000
24	FE 1 YZ	0.000000	0.000000	0.000055	-0.000083	0.000000
25	FE 2 S	0.000373	0.000000	0.000000	0.000000	0.000290
26	FE 2 S	0.001206	0.000000	0.000000	-0.000001	0.000983
27	FE 2 S	0.000628	0.000000	0.000000	-0.000002	0.002867
28	FE 2 X	0.000028	0.000016	0.000000	0.000000	0.000008
29	FE 2 Y	-0.000028	0.000016	0.000000	0.000000	-0.000008
30	FE 2 Z	0.000000	0.000000	-0.000061	0.000062	0.000000
31	FE 2 X	-0.001249	-0.001385	0.000000	0.000000	-0.000563
32	FE 2 Y	0.001249	-0.001385	0.000000	0.000000	0.000563

33	FE 2	Z	0.000000	0.000000	0.002656	-0.002891	-0.000002
34	FE 2	X	0.000161	0.000191	0.000000	0.000000	-0.000435
35	FE 2	Y	-0.000161	0.000191	0.000000	0.000000	0.000435
36	FE 2	Z	0.000000	0.000000	-0.000206	0.000414	0.000000
37	FE 2	XX	-0.000040	-0.000154	0.000000	0.000000	0.000072
38	FE 2	YY	-0.000040	0.000154	0.000000	0.000000	0.000072
39	FE 2	ZZ	0.000081	0.000000	0.000000	0.000000	-0.000144
40	FE 2	XY	-0.000016	0.000000	0.000000	0.000000	0.000006
41	FE 2	XZ	0.000000	0.000000	-0.000007	-0.000015	0.000000
42	FE 2	YZ	0.000000	0.000000	0.000007	0.000015	0.000000
43	FE 2	XX	0.000427	0.001487	0.000000	0.000001	-0.000687
44	FE 2	YY	0.000427	-0.001487	0.000000	0.000001	-0.000687
45	FE 2	ZZ	-0.000855	0.000000	0.000000	-0.000001	0.001375
46	FE 2	XY	0.000104	0.000000	0.000000	0.000000	-0.000048
47	FE 2	XZ	0.000000	0.000000	0.000055	0.000083	0.000000
48	FE 2	YZ	0.000000	0.000000	-0.000055	-0.000083	0.000000

...

Similarly, if you were interested in calculated U and J for atom 2 of the system in *test/fe2o10/hem2.inp*, you would put the limits at 37 and 48 instead.

Caution: when diffuse basis functions are used, special attention is needed for selecting the d basis functions to calculate the occupation numbers, which is obtained through Mulliken population analysis. Below are the d basis functions in the Stuttgart basis set on iron.

...

D	4		
1	33.66679000	0.0365290000	
2	10.23569500	0.1828250000	
3	3.466488000	0.4370690000	
4	1.127296000	0.5751780000	
D	1		
1	0.3082470000	1.0000000000	
D	1		
1	0.0800000000	1.0000000000	

...

The third set is very diffuse with the exponent of the Gaussian function being 0.08. In this case, the peak of the basis function is near the bonding region of Fe and O. Thus, it should not be adopted for population evaluation of localized d electrons, which means that the basis functions specified in the OrbsAA file should exclude the third set of d basis functions in this example.

Step 2. Run the calculation

Run GAMESS-UJ in the directory that contains the input and OrbsAA files.

Step 3. Find U and J in the output

After the calculation is finished, open the output file and search for the section starting 'Found OrbsAA'. This will be followed by a section like:

Found OrbsAA

populations of d orbitals

orb	alpha	beta
D1	1.0016	0.0574
D2	1.0056	0.0584
D3	1.0115	1.0103
D4	1.0131	0.0310
D5	1.0131	0.0310
D6	0.0000	0.0000

d-d interactions:

A-A:	10.1806
B-B:	0.1911
A-B:	5.9936

denominators:

U:	16.3653
J:	10.3717

The numbers under the title populations of d orbitals correspond to the populations of the d orbitals with different magnetic numbers. The sixth value (D6) should be zero, as there should only be five d orbitals and the sixth is an artifact of how GAMESS uses spherical harmonics. If D6 is not equal to zero, you will get a warning indicating that something is wrong with the calculation. Most likely, you specified the wrong limits in the OrbsAA file. Note that due to the approximate nature of the Mulliken population analysis used to get these values, some orbitals can have occupation numbers of greater than 1.

To find U and J , go to the section titled 'SUMMARY OF INTEGRALS'. This section is pretty much self-explanatory.

```
=====
=====
!!                               !!
!!           SUMMARY OF INTEGRALS           !!
!!                               !!
-----

U [au] [eV]:    0.3532    9.6061
J [au] [eV]:    0.0342    0.9297
```

U-J [au] [eV]: 0.3190 8.6764

Now you are done with the calculation of U and J .

IV. References

1. N. J. Mosey and E. A. Carter, "Ab initio Evaluation of Coulomb and Exchange Parameters for DFT+U Calculations," *Phys. Rev. B.*, **76**, 155123 (2007).
2. N. J. Mosey, P. Liao, and E. A. Carter, "Rotationally-Invariant *ab initio* Evaluation of Coulomb and Exchange Parameters for DFT + U Calculations," *J. Chem. Phys.*, **129**, 014103 (2008).