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|
|   Generalized Product Function Energy Partitioning - GPF-EP
|   Version 0.6 - March, 2016
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1. INTRODUCTION

1.1 WHAT IS GPF-EP?

In simple words, the Generalized Product Function Energy Partitioning (GPF-EP) is a powerful Energy Decomposition Analysis (EDA) scheme suited for studying the nature of the chemical bond in molecular systems. The method is based on the original density-based energy decomposition first proposed by Ruedenberg [1]. Electron densities are separated in a quasi-classical part, which can be mostly interpreted classically, and an interference part, which accounts for quantum interference between one-electron eigenstates. GPF-EP is an adaptation of Rudenberg's original framework to the GPF wave functions, developed by McWeeny [2]. A GPF wave function consists of a strongly orthogonal product of smaller wave functions of electron subspaces (groups) of a molecular system, and its reduced density matrices (RDMs) consist of intergroup and intragroup parts. This particular structure of the RDMs of GPF wave functions allows the energy partitioning to be carried out for individual bonds and bond groups. The interpretation of the results is facilitated by the use of modern VB functions such as Generalized Valence Bond (GVB) [3] or Spin Coupled Valence Bond (SCVB)[4], since these methods naturally generate uniquely determined quasi-atomic orbitals, allowing direct correspondence between results and chemical structures (atoms connected by chemical bonds). This choice of group wave functions also precludes the selection of criteria for atomic orbital generation, which is arbitrary in Ruedenberg's original work. For more details, the program user should read the references related to GPF-EP [5-14], specially the last review published recently [15].

2. ABOUT THE PROGRAM

2.1. FEATURES

At the present version (0.6), the GPF-EP program exists as a module of the VB2000 code.

GPFEP allows to partition the total energy of an atomic or molecular system to various contributions, as described in the GPF-EP papers [5]. It is also possible to partition the electric dipole moment of a

molecule in the quasi-classical and interference contributions for each electron group (in a GPF calculation) [16].

An additional script to generate contour maps of the electronic density and its partitions is under development.

2.2 LICENSE AND CITATION

Since the atual version of GPF-EP is officially incorporated into VB2000, the same license of this program should apply as well to GPF-EP. We highlight that any commercial use of the code is not allowed and all scientific work using the GPFEP code must cite the proper references described below.

Publications with results obtained from using VB2000 should cite the software and the theory in the following way:

Theory:

- (a) Cardozo, T.M.; Nascimento, M.A.C. Energy partitioning for generalized product functions: the interference contribution to the energy of generalized valence bond and spin coupled wave functions. J. Chem. Phys. 2009, 130, 104102. [5]
- (b) Cardozo, T.M.; Nascimento, M.A.C. Chemical Bonding in the N₂ Molecule and the Role of the Quantum Mechanical Interference Effect. J. Phys. Chem. A 2009, 113, 12541-8. [6]

2.3 CHANGELOG

> Version 0.1 - July 2009 written in the VB2000/GAMESS framework by TMC
Reorganization of the code and easier installation into VB2000/GAMESS by CEVM

- > Version 0.2 - June 2015 updated by DWOS
 - * Calculation of occupation numbers
 - * Generalization of the equations to include SCVB(N,M) groups
 - * Simple error handling and warning messages
 - * Friendly printing of results in the outfiles
 - * Fixed: print pair interference energies for more than one group

- > Version 0.3 - September 2015 updated by DWOS
 - * Implementation of Dipole Moment Partitioning
 - * Correction of warnings

- > Version 0.4 - September 2015 updated by DWOS
 - * Updated COMMON blocks for VB2000 version 2.7 / GAMESS 2014
 - * Removed dummy input variable from RGMST routine
 - * Print orbital occupations only if there is a SCVB(N,M) group

- > Version 0.5 - January 2016 updated by DWOS
 - * Fixed: don't skip GPFDP if print occupations
 - * Fixed: version label for output file

- > Version 0.6 - March 2016 updated by DWOS
 - * Comments in the code and Documentation

*Some minor bugs fixed (thanks to Brian J. Duke)

4. INSTALLATION

At the present version (0.6), the GPF-EP program exists as a module of the VB2000 code. Thus, it will be installed together with VB2000. See VB2000 manual for instructions.

5. HOW TO USE

In order to execute GPF-EP, the user should include the keyword \$GPFEP in the VB2000 input file. In the following line, one can specify two filenames, respectively, for the Energy Partitioning and the Density Matrix raw text files, which are generated at the end of the calculation. If not specified, the calculation will generate automatically the files 'JOBNAME.part' and 'JOBNAME.dmat' where JOBNAME is the name of the input file.

Additionally, if one want to calculate electric dipole moment partitioning into quasi-classical and interference contributions you must include the keyword \$GPFDP besides the \$GPFEP one. For example the last few lines of your input file could be like the following:

```
$GPFEP
partition.txt dmatrix.txt

$GPFDP
```

6. EXAMPLES

VB2000 has a lot of different features and types of calculations available. Here we present the expected behavior of the GPFEP module in each of the possible cases.

It is important to read the VB2000 manual in order to be familiarized with how the program works and how to construct a GPF wave function for a given molecule. We use the terminology of the VB2000 manual related to the general control (\$GENCTL) variables in the input file.

a) a simple HF calculation, i.e. GPF(1) with METHOD(1) = 1

In this case there it is pointless to calculate interference energies, so if the keyword \$GPFEP is present, the GPFEP module aborts the calculation.

b) if there are more than one HF group

In general, there is no necessity of create two or more separate HF groups, since they are used for describe electrons which are not directly involved in bonding, such as core and lone pair electrons. So, if the keyword \$GPFEP is present, the GPFEP module aborts the calculation.

c) a VBSCF calculation, i.e. one of the groups has METHOD(i)=2

In our experience, one must be careful in carrying out the energy partitioning because an inadequate choice of the VB structures (set in \$##VBSTR) might yield unphysical energy results. The output of the energy partitioning should exhibit a warning concerning that.

d) a GVB-PP calculation

In order to perform a GVB-PP calculation, the valence space of the molecule should be split in groups of two electrons, treated by SC (METHOD=3). The output of the energy partitioning should print the different energy terms for each group, the intergroup contributions of the energy and the partitioning of the total energy.

e) a SCVB or CASVB calculation (METHOD=3 or 4)

When a SC or CASVB group with more than 2 electrons is present, the output information includes also the interference energies between each pair of orbitals within the group, for each SC group.

If the number of electrons is different from the number of the orbitals of the SC group, it is a SCVB(N,M) calculation. The output will show also the orbital occupations of each orbital in the group.

It is worth noticing that if the \$GPFDP keyword is present, the energy partitioning output will also show the information concerning the electric dipole moment partitioning.

There is one attached example input file of the H₂O molecule in GVB-PP/6-31G* level ("vb-exam42.inp"). The expected results are in attached files as well ("vb-exam42.part.bkp" and "vb-exam42.dmat.bkp").

Some hints and quick tips in order to get better results will become available soon in a next version of the manual.

Any doubts, suggestions and questions may be sent by e-mail to M.Sc. David W. O. Sousa (david@pos.iq.ufrj.br) or Prof. Thiago M. Cardozo (thiago.dfq@gmail.com).

7. ACKNOWLEDGEMENTS

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