Project Title: System Verification and Validation Plan for EOMEE

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1 Revision History

Date	Version	Notes
29-10-2020	1.0	Created VnV first draft

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2 Symbols, Abbreviations and Acronyms

symbol	description
Т	Test
VnV	Verification and Validation
DD	Data Definition
EOMEE	Equation-of-motion for excited states
IM	Instance Model
MO	Molecular orbital(s)
HOMO	Highest Occupied Molecular Orbital
LUMO	Lowest Unoccupied Molecular Orbital
R	Requirement
SRS	Software Requirements Specification
RDM	Reduced density matrix
TDM	Transition density matrix
h_{pq}	1-electron integral
v_{pqrs}	2-electron integral
γ_{pq}	1-electron reduced density matrix
Γ_{pqrs}	2-electron reduced density matrix

include a link to your on for EOMEE. First, the strategies

This document presents the VnV plan for EOMEE. First, the strategies for the verifycation of the SRS, code desing and implementation will be described, followed by the software validation plan. The later one will present the system and unit tests that will verify the functional and nonfunctional requirements of the package.

3 General Information

3.1 Summary

The present document presents the validation plan of the package Equation of Motion for Excited States (EOMEE). This program is intended as a research tool for evaluating excited states (including ionizad states) and their related spectroscopic properties such as the oscillator strengths. It also strives to assess the effect of the electron correlation on these properties.

3.2 Objectives

The present document's aim is to build confidence in the software by designing tests that verify its correctness (compliance with the requirements). Validation of the inputs and outputs or the code usability will be among the main tests this plan will be focusing on.

3.3 Relevant Documentation

Through this document we will be referring to the requirement specifications for EOMEE[Sanchez-Diaz (2020)], in particular to its functional and non-functional requirements.

4 Plan

4.1 Verification and Validation Team

The review of EOMEE will be conducted by the following parties:

 The Ayers Lab members, in particular Michael Rischer, Dr. Paul Ayers and Gabriela Sánchez Díaz.

- Dr. Spencer Smith.
- Members of 2020 CAS741 course; in particular the following responsibilities have been defined:

Mohamed AbuElAla (Primary Reviewer)

Seyed Parsa Tayefeh Morsal (SRS Reviewer)

Ting-Yu Wu (VnV Reviewer)

Xuanming Yan (MG and MIS Reviewer)

SRS Verification Plan 4.2

The software requirement specifications (SRS) verification will be carried by the reviewers following the indications describes in the SRS verification test. This test is intended as a guide in the revision process

4.3 Design Verification Plan

The modules design will be discussed with the review team members Dr. Paul Ayers and Michael Richer. It will also be presented to/evaluated by Dr. Smith and the members of 2020 CAS741 course.

4.4 Implementation Verification Plan

The implementation will be verified through system and unit testing. The following test areas will be defined:

- Subsection 5.1.1 Input Verification: includes checks for the input variables types and values.
- Subsection 5.1.2 Energies and TDMs Evaluation: tests in which the properties represented by the instance models (IM1-IM6) are evaluated and compared against literature or pseudo-oracle results.
- Subsection 5.2.1 SRS Review: introduces a questionnaire to guide the SRS review team.
- Subsection 5.2.2 Usability Verification Plan: tests with the purpose of identifying potential deficiencies in the user-software interaction.

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• Subsection 5.2.3 Performance: an assessment atemp at the numerical stability limits of the implemented IM1-IM5.

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The corresponding sections for the unit tests will be added once that section of the VnV plan is completed —Author]

4.5 Automated Testing and Verification Tools

We will be using Pytest testing framework for tests automation with the plugin pytest-cov to determine the code coverage percentage. Additionally, the following tools will be used to enforce compliance with Python style conventions for code and documentation:

- Pylint, Flake8 and Black as Python linters. The last one is also a code auto-formatter.
- flake8-docstrings as a static analysis for Python docstring conventions.

For continuous integration we will use the Travis-CI tool.

Software Validation Plan

Have you had success in setting the system follow This first

To assess the validity of EC

tests, these will be compare
for electronic structure calcu
source for validation can be t
and NIST ASD Team (2019)

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5 System T To assess the validity of EOMEE results, in particular during the system tests, these will be compared against the ones obtained with the package for electronic structure calculations Gaussian Frisch et al. (2016). Another source for validation can be the NIST Atomic Spectra Database A. Kramida and NIST ASD Team (2019)].

System Test Description 5

5.1Tests for Functional Requirements

The tests described in the following subsections check functional requirements listed in the subsection 5.1 of the SRS, in particular requirements R1 and R2 about the input variables and R4 and R5 related to the spectroscopic properties evaluated by EOMEE.

3

5.1.1 Input Verification

Input type and value

1. input-type:IT

Control: Automatic Initial State: N/A

Input: Two sets of inputs, corresponding to the one-electron integral, two-electron integral, one-electron reduced density matrix and two-electron reduced density matrix, will be provided according to Table 1:

Input set	S1	S2		
h_{pq}	tuple	2-idx numpy array		
v_{pqrs}	4-idx numpy array	4-idx numpy array		
γ_{pq}	2-idx numpy array	2-idx list		
Γ_{pqrs}	4-idx numpy array	4-idx numpy array		
Wrong	tuple variable	list variable		

Table 1: Type of the input variables

The variables in the table will be defined as:

tuple: ((1,2), (3,4))

2-idx numpy array: numpy.random.rand(4, 4).astype(float)

2-idx list: [[1.0, 2.0],[3.0, 4.0]]

4-idx numpy array: numpy.random.rand(4, 4, 4, 4).astype(float)

Output: A type-error will be raised in each case.

Test Case Derivation: N/A

How test will be performed: The test module will feed the inputs, as specified in Table 1, to the EOMEE code and verify that a type-error message is raised.

2. input-value:IV

Control: Automatic

Do you need

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Initial State: N/A

Input: Five input sets, corresponding to the one-electron integral, two-electron integral, one-electron reduced density matrix and two-electron reduced density matrix, as described in Table 2.

Input set	S1	S2	S3 S4		S5	
h_{pq}	v_{pqrs}	h_{pq}	$A_{(n \times m)}$	$A_{(m \times m)}$	γ_{pq}	
v_{pqrs}	h_{pq}	v_{pqrs}	$B_{(n\times m\times m\times m)}$	$B_{(n \times n \times n \times n)}$	Γ_{pqrs}	
γ_{pq}	γ_{pq}	Γ_{pqrs}	$A_{(n \times m)}$	$C_{(n\times n)}$	h_{pq}	
Γ_{pqrs}	Γ_{pqrs}	γ_{pq}	$B_{(n \times m \times m \times m)}$	$D_{(n\times n\times n\times n)}$	v_{pqrs}	
Wrong	array dimensions		array shape		RDMs constrains	

Table 2: Test input variables definition.

The variables in Table 2 will be defined as:

 h_{pq} : numpy.random.rand(4, 4).astype(float)

 v_{pqrs} and $B_{(n \times n \times n \times n)}$: numpy.random.rand(4, 4, 4, 4).astype(float)

 γ_{pq} and $C_{n\times n}$: numpy.asarray([[1,0,0,0], [0,0,0,0], [0,0,1,0], [0,0,0,0]])

 Γ_{pqrs} and $D_{(n\times n\times n\times n)}$: $\gamma_{pr}\otimes\gamma_{qs}-\gamma_{ps}\otimes\gamma_{qr}$

 $A_{(n \times m)}$: numpy.random.rand(4, 3).astype(float)

 $B_{(n \times m \times m \times m)}$: numpy.random.rand(4, 3, 3, 3).astype(float)

 $A_{(m \times m)}$: numpy.random.rand(6, 6).astype(float)

Output: The EOMEE code must raise a value error for each case specified in Table 2.

Test Case Derivation: Input cases S1 and S2 target incorrect dimensions in the electron integrals or RDMs. S3 verifies that h_{pq} and \sqrt{pq} are square matrices, while v_{pqrs} and Γ_{pqrs} must be tensors, each with equal numbers of rows and columns. Mismatching number of spinorbitals in input parameters (given by the array shapes) is verified by the test case S4. The last column input set targets the requirement R2 in the SRS relative to the physical constraints of the RDMs.

How test will be performed: The test cases in Table 2 are passed to the EOMEE code by the testing framework which will also verify that a value-error message is raised.

5.1.2 Energies and TDMs Evaluation

Transition energies

The tests described under this section require the one- and two-electron integrlas for the N-electron, M-atom system to be stored in the directory test/data as NumPy's binary files (.npy). Unless otherwise stated, for each implemented EOM method (IM1-IM5, SRS subsection 4.2.5), the lowest (positive valued) transition energy will be taken and compared against an 'lexpected" value (generally from a Gaussian Frisch et al. (2016)] calculation). Because at this point we are not targeting the performance of the methods, only small systems with at most 5 electrons and 10 molecular orbitals (MOs) were included in the test cases bellow. We will use the absolute error ($|E_{IM\#} - E_{expected}|$) to measure the method's accuracy.

1. correct-lowest-transition:LT Can you use relative error 1 preferable

Control: Automatic Initial State: N/A

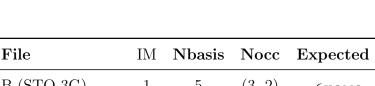
Input: The one- and two-electron integrals corresponding to the systems presented in Table 3, the tolerance value 1.0×10^{-6} .

Table 3 contains the test cases description. All systems have closed-shell electronic configurations except the boron atom (B).

Output: Eigenvalues (and eigenvectors) solution to the IMs.

Test Case Derivation: The one- and two-reduced density matrices required as input by the EOMEE methods will be generated from the number of electrons (Nocc) and MOs (Nbasis). Because the ground state wavefunction (Ψ_0) for the systems in Table 3 will be modeled by a single Slater determinant (specifically the lowest energy Hartree-Fock Slater determinant), the one- and two-RDMs can be defined as:

$$\gamma_{pq} = \begin{cases} \delta_{pq} & p, q \in \text{occupied MO} \\ 0 & \text{virtual MO} \end{cases}$$
$$\Gamma_{pqrs} = \frac{1}{\sqrt{2}} (\gamma_{pr} \gamma_{qs} - \gamma_{ps} \gamma_{qr})$$



B (STO-3G)	1	5	(3, 2)	$-\epsilon_{HOMO}$
B (STO-3G)	2	5	(3, 2)	ϵ_{LUMO}
He (cc -pVDZ)	1	5	(1, 1)	$-\epsilon_{HOMO}$
He (cc -pVDZ)	2	5	(1, 1)	ϵ_{LUMO}
HeH^+ (STO-3G)	1	2	(1, 1)	$-\epsilon_{HOMO}$
HeH^+ (STO-3G)	2	2	(1, 1)	ϵ_{LUMO}
HeH^+ (STO-3G)	3	2	(1, 1)	0.91123209
H_2 (STO-6G)	4	2	(1, 1)	1.83843430

Table 3: Input variables. The reference energy values (last column) are in Hartree.

File	ϵ_{HOMO}	ϵ_{LUMO}	
B (STO-3G)	-0.20051823	0.29136562	
He (cc-pVDZ)	-0.91414765	1.39744193	
HeH^+ (STO-3G)	-1.52378328	-0.26764028	

Table 4: Frontier molecular orbital energies in Hartree.

How test will be performed: The testing framework will pass the electron integrals and density matrices to the EOM method (IM column in Table 3). From the solutions, the lowest transition energy will be determined and compared against the "expected" value. If the absolute error is less or equal than the tolerance criteria, the test will pass.

Transition Density Matrices

1. matrix-symmetry:TS

Control: Automatic

Initial State: The EOM method (IM1-IM5) has been solved.

Input: The following input arrays located in the test/data folder:

- be_sto3g_twoint_genzd_anti.npy
- 2dm_be_sto3g_genzd_anti.npy
- be_sto3g_oneint_genzd.npy
- 1dm_be_sto3g_genzd.npy

The expansion coefficients matrix and the lowest nonzero excited state index.

Output: The TDM for the selected state.

Test Case Derivation: The equations to evaluate the TDMs corresponding to each EOM method can be found in the SRS (subsection 4.2.5, IM6).

How test will be performed: The test framework will pass the specified inputs to a function that evaluates the EOMEE methods and TDMs. The selected TDM and its transpose will be compared using NumPy's allclose method. The test will pass if the matrix is asymmetric.

5.2 Tests for Nonfunctional Requirements

The tests described in the following subsections verify the nonfunctional requirements listed in the subsection 5.2 of the SRS.

5.2.1 SRS Review

1. SRS_questionnaire:SQ

Type: Manual

Initial State: N/A

Input/Condition: The the SRS document [Sanchez-Diaz (2020)] will be provided to Dr. Ayers, Dr. Smith, Mohamed AbuElAla and Gabriela Sánchez along with a questionnaire (to be found in the Appendix section).

Output/Result: GitHub issues

How test will be performed: The reviewers will read the document and questions and report any problems or inconsistencies.

5.2.2 Usability verification

Portability and usability tests

1. installability-test:PT

Type: Manual

Initial State: The may or may not be some Python program and modules already installed.

Input/Condition: Internet connection and some web browser available.

Output/Result: EOMEE module installed or issue reported in GitHub.

How test will be performed: The GitHub repository will be cloned by Gabriela Sánchez in different platforms (Ubuntu Focal Fossa, Mac OS Catalina and Windows 10). The installation will follow the instructions in the README.md file located on the repository root folder. Upon installation completion the system and unit tests will be ran.

2. usability-test:UT

Type: Manual.

Initial State: The EOMEE code may or not be installed on the user's computer.

Input/Condition: Members of the test team, the link to the project's GitHub repository and the following example input files for the beryllium atom: Me and specific

- be_sto3g_twoint_genzd_anti.npy
- 2dm_be_sto3g_genzd_anti.npy
- be_sto3g_oneint_genzd.npy
- 1dm_be_sto3g_genzd.npy

These files will be located in the test/data folder.

Output/Result: Users response to the usability survey found in the Appendix section.

How test will be performed: The users will clone the repository and install the program. Using the provided input files they will choose to evaluate one of the following properties for Be: ionization potential, electron affinity or electron excitation. Additionally, they will determine the TDMs for their selected method. After completing these tasks the test team will fill out the survey.

5.2.3 Performance

Numerical instability

1. illconditioning-test:NIT

Type: automatic Initial State: N/A

Input/Condition: A matrix orthogonalization methods (strings symmetric or asymmetric), threshold values in the range $1.0 \times 10^{-4} - 1.0 \times 10^{-9}$, the example input files from the usability-test and the instance models IM1 to IM5 (SRS subsection 4.2.5).

Output/Result: A graph showing how the lowest nonzero value for instance models IM1-IM5 changes with the tolerance value.

How test will be performed: The test framework will pass the inputs to EOMEE and a graph will be generated.

5.3 Traceability Between Test Cases and Requirements

Table 5 shows what requirement specifications the functional and nonnfunctional system tests address:

6 Unit Test Description

[Reference your MIS and explain your overall philosophy for test case selection. —SS] [This section should not be filled in until after the MIS has been completed. —SS]

6.1 Unit Testing Scope

[What modules are outside of the scope. If there are modules that are developed by someone else, then you would say here if you aren't planning on

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	IT	IV	LT	TS	SQ	PT	UT	NIT
R1	X	X						
R2		X						
R3								
R4			X	X				
R5			X	X				
R6								
Reusable								
Usable						X	X	
Portable						X		
Correct			X	X	X			

Table 5: Traceability for system tests and requirements

verifying them. There may also be modules that are part of your software, but have a lower priority for verification than others. If this is the case, explain your rationale for the ranking of module importance. —SS

6.2 Tests for Functional Requirements

[Most of the verification will be through automated unit testing. If appropriate specific modules can be verified by a non-testing based technique. That can also be documented in this section. —SS]

6.2.1 Module 1

[Include a blurb here to explain why the subsections below cover the module. References to the MIS would be good. You will want tests from a black box perspective and from a white box perspective. Explain to the reader how the tests were selected. —SS]

1. test-id1

Type: [Functional, Dynamic, Manual, Automatic, Static etc. Most will be automatic —SS]

```
Initial State:
  Input:
  Output: [The expected result for the given inputs—SS]
  Test Case Derivation: [Justify the expected value given in the Output
  field —SS
  How test will be performed:
2. test-id2
  Type: [Functional, Dynamic, Manual, Automatic, Static etc. Most will
  be automatic —SS]
  Initial State:
  Input:
  Output: [The expected result for the given inputs—SS]
  Test Case Derivation: [Justify the expected value given in the Output
  field —SS]
  How test will be performed:
3. ...
```

6.2.2 Module 2

...

6.3 Tests for Nonfunctional Requirements

[If there is a module that needs to be independently assessed for performance, those test cases can go here. In some projects, planning for nonfunctional tests of units will not be that relevant. —SS]

[These tests may involve collecting performance data from previously mentioned functional tests. —SS]

6.3.1 Module?

1. test-id1

Type: [Functional, Dynamic, Manual, Automatic, Static etc. Most will be automatic —SS]

Initial State:

Input/Condition:

Output/Result:

How test will be performed:

2. test-id2

Type: Functional, Dynamic, Manual, Static etc.

Initial State:

Input:

Output:

How test will be performed:

6.3.2 Module?

...

6.4 Traceability Between Test Cases and Modules

[Provide evidence that all of the modules have been considered. —SS]

References

J. Reader A. Kramida, Yu. Ralchenko and NIST ASD Team. NIST Atomic Spectra Database (ver. 5.7.1), [Online]. Available: https://physics.nist.gov/asd [2017, April 9]. National Institute of Standards and Technology, Gaithersburg, MD., 2019.

M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox. Gaussian 16 Revision C.01, 2016. Gaussian Inc. Wallingford CT.

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Malavika Srinivasan and Spencer Smith. Task list for scientists-srs review. https://gitlab.cas.mcmaster.ca/smiths/cas741/-/tree/master/Examples/DocumentReviewPlans, 2017. Accessed: 2020-10-29.

7 Appendix

7.1 Symbolic Parameters

The definition of the test cases will call for SYMBOLIC_CONSTANTS. Their values are defined in this section for easy maintenance.

7.2 Usability Survey Questions

- 1. Were the installation instructions for your platform clear? Could you successfully install EOMEE by following them?
- 2. Was the code's documentation helpful when learning how to run the calculations?
- 3. Did you look at the tests files when learning how to run the calculations? Were they helpful?
- 4. Could you successfully run an excited state calculation?
- 5. Could you successfully determine the transition density matrices for your chosen EOM method?
- 6. Was the naming of the functions descriptive (it was clear the task they were supposed to perform)?
- 7. Do you have any improvement suggestions regarding the documentation or code?
- 8. How would you rate the learning curve for this software? (Very easy, easy, hard, very hard)

7.3 SRS Questionnaire

Because the members of the VnV team might have limited time to review the document some of the question bellow have been specifically assigned:

- 1. Are the energy units in the Table of units (section 1.2) appropriate for the physical problems EOMEE addresses?
- 2. Was the Table of Symbols (section 1.2) complete?

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- 3. Does the used notation in the Table of Symbols (section 1.2) matches the one generally used in the literature? [Dr. Ayers]
- 4. Were the abbreviations and acronyms (section 1.3) properly used through the document?
- 5. Is Figure 1 for the system context (section 3.1) along with its description correct? Do the listed user and software responsibilities make sense? [Dr. Smith and Mohamed AbuElAla]
- 6. Was the description of the problem EOMEE intends to solve clear? Were all the terminology definitions needed for the understanding of subsequent sections included? (sections 4.1 and 4.1.1) [Dr. Smith and Mohamed AbuElAla]
- 7. Were the terminology definitions listed in section 4.1.1 correct? [Dr. Ayers]
- 8. Is section 4.1.2 (Physical System Description) clear? Do you have any suggestions that might help improve the understanding of EOMEE's physical system? [Mohamed AbuElAla]
- 9. Were all assumptions pertinent to the EOM models included? Are the ones listed correct?(section 4.2.1) [Dr. Ayers]
- 10. Were the connections between the assumptions and the appropriate IM, GS, DD, T or LC included? (section 4.2.1)
- 11. Were the defined theoretical models the correct general equations that EOMEE is based on? Were the descriptions and derivations appropriate? (section 4.2.2) [Dr. Ayers]
- 12. In section 4.2.3, are the definitions of the transition operator and EOM approximations correct? Are the descriptions and derivations appropriate? [Dr. Ayers]
- 13. Are DD2, DD3, DD4 and DD5 properly described? Are the presented symmetry properties of DD3 and DD5 correct? (section 4.2.4) [Dr. Ayers]
- 14. Are the IMs inputs and outputs appropriate? (section 4.2.5) [Dr. Smith]

- 15. After reading the Input Data Constraints section (4.2.6), are the physical constraints presented in the Table 1 correct? Are the typical values assigned to the one- and two-electron integrals reasonable? What changes do you suggested making to the values presented in this table? [Dr. Ayers]
- 16. Do the output constraints presented in Table 3 (section 4.2.7) make sense? If not, could you suggest changes to be made? [Dr. Ayers]
- 17. Do the listed Functional and Nonfunctional Requirements make sense (sections 5.1 and 5.2 respectively) [Dr. Smith]
- 18. Were the cross-references made correctly through the document? [Mohamed AbuElAla]

These questions are inspired on the SRS review plans by Malavika Srinivasan and Spencer Smith [Srinivasan and Smith (2017)].