Usage Report for Fiscal Year 2024

Project Title:

Exploring the use of Pair-Natural Orbitals for Time-Domain Coupled-Cluster

Name:
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1. Background and purpose of the project, relationship of the project with other projects

Time-Domain Coupled-Cluster can provide valuable insight into the excited states of molecular systems. It is especially useful in describing the states that are otherwise difficult to describe in the frequency domain such as high energy states or systems with a high density of states. As such it is particularly useful for the description of high energy processes such as X-Ray Near Edge Absorption Spectroscopy.

It is however held back by its cost, Coupled-cluster is an accurate but expensive electronic structure method(scales $O(N^6)$) made more expensive in the time-domain as it requires the calculation of many tens of thousands of time steps to resolve a spectra to a reasonable degree. This issue is further compounded in the high energy ranges as in order to accurately describe the absorption range very minute time steps are required adding another difficulty to the calculation of interesting systems, i.e. metal complex L-edge absorption. This project aims to implement and test the viability of Pair Natural Orbitals which have been shown to reduce the cost of ground state Coupled Cluster calculations by up to 99% within the time-domain framework.

2. Specific usage status of the system and calculation method

Psi4 is an open-source package for electronic structure calculations, with a wide range of capabilities. Psi4 was used to perform the ground state Coupled-cluster calculation. The results of the ground state calculations were then used in Python code to prepare and perform the time-propagation for the excited properties.

3. Result

Hokusai allowed for the calculation of larger systems to validate the initial Time-Dependent Coupled-cluster implementation in cases more difficult than could be calculated using local machines. This provided further evidence that the initial implementation was complete and without errors that would be problematic when testing more advanced algorithms like the PNO method being implemented.

4. Conclusion

The use of Hokusai is invaluable for the calculation of systems that are too large to be feasible for local machines and as such will be useful in the coming year for running the testing and validation of the PNO based Time-dependent Coupled-cluster implementation under construction.

5. Schedule and prospect for the future

In the following year Hokusai will be used to verify the implementation and cost reduction of the new PNO implementation for systems that are too costly and large to run on smaller local machines.

6. If no job was executed, specify the reason.

N/A