OOKAMI PROJECT APPLICATION

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Project Title: Molecular Dynamics and Molecular Response

Usage: Testbed

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Usage Description:

With support from NSF and DOE, we have implemented a TDDFT linear response module in NWChem, and extended its functionality over the years. [1–3] We use this response module to study molecular properties such as optical rotation, polarizability, Raman optical activity, and others, [4–6], and how they are influenced by the dynamics of a system such as a solvated chromophore. Underlying molecular dynamics (MD) simulations are typically performed at the DFT level with QuantumEspresso (QE), while the response calculations are done with NWChem for a number (usually between 256 to 1024) configurations taken from the MD production phase.

The parallel performance of the DFT / TDDFT single point and response code of NWChem, in particular, in these calculations creates a bottleneck, even if the calculation runs only on a single multi-core node. I suspect this must be, at least in part, due to limitations regarding the communication among the node's CPU cores. I attended an Ookami webinar on March 3, 2021, and it seems to me that the Ookami hardware could potentially offer large speed-up of the response calculations compared to the computing capabilities that we have available elsewhere (mainly at the University at Buffalo's Center for Computational Research [CCR]). I would also like to test if the time-consuming (real time and CPU time) MD simulations can be done much faster on Ookami. Finally, I would like to work with the Ookami team to improve the multi-node performance of the NWChem DFT/TDDFT response functionality, if this is possible.

As an application, I would like to study the optical rotation (OR) of norbornenone in solution. This molecule has been an enigma to the optical activity community for many decades. [4] It has a huge OR (about 1200 deg / [cm^2 dmol]) in solution, with relatively minor variations as a function of solvent, but only about half that in gas phase. So far, efforts to reproduce the solution phase OR by computations, for the right reasons, have been unsuccessful.

Computational Resources:

- Total node hours per year: 10,000
- Size (nodes) and duration (hours) for a typical batch job: 8 to 9 hours on 1 to 4 nodes
- Disk space
  Home: Default (30 GB) will be sufficient
  Project: Default (100 GB) will be sufficient.
  Scratch: Likely not to exceed a few GB per running job. No special accommodations needed.

Personnel Resources:

My team and I are familiar with SLURM, environment modules, compiling code etc., so training for users will likely not be needed. We may need some help with getting NWChem and QE running first, and up to speed next.

Required software:

Fortran and C / C++ compilers, MPI and related libraries. Optimized Blas, Lapack would be useful.

If your research is supported by US federal agencies:

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References

[1] Autschbach, J. Time-dependent density functional theory for calculating origin-independent optical rotation and rotatory strength tensors. *ChemPhysChem* **2011**, *12*, 3224–3235.

[2] Hammond, J. R.; Govind, N.; Kowalski, K.; Autschbach, J.; Xantheas, S. S. Accurate dipole polarizabilities for water clusters n=2-12 at the coupled-cluster level of theory and benchmarking of various density functionals. *J. Chem. Phys.* **2009**, *131*, 214103.

[3] Aprà, E. *et al.* NWChem: Past, present, and future. *J. Chem. Phys.* **2020**, *152*, 184102.

[4] Moore II, B.; Srebro, M.; Autschbach, J. Analysis of optical activity in terms of bonds and lone-pairs: The exceptionally large optical rotation of norbornenone. *J. Chem. Theory Comput.* **2012**, *8*, 4336–4346.

[5] Autschbach, J.; Srebro, M. Delocalization error and 'functional tuning' in Kohn-Sham calculations of molecular properties. *Acc. Chem. Res.* **2014**, *47*, 2592–2602.

[6] Abella, L.; Ludowieg, H. D.; Autschbach, J. Theoretical Study of the Raman Optical Activity Spectra of $[M(en)_3]^{3+}$ with M = Co, Rh. *Chirality* **2020**, *32 (Koji Nakanishi special issue)*, 741–752.