Report on the faculty development grant, July-August 2021.

"Exploring novel Green's function-based *ab initio* methods for the prediction of optical properties of molecules"

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1. Introduction

This faculty development project is a feasibility study for a new computational physics method, including analysis of assumptions, complexity, numerical algorithms, and their parallel implementation. Computer codes will be produced when time permits. In engineering terms, this is a 'conceptual design'. The budget for this project was $3,000.

2. Overview of previous work

The PI had some former experience with ab initio calculations back in 2006-2008. His projects included: calculation of optical properties of MgB_2 and SiC using ABINIT software and the analysis of algorithms used by 'beyond-DFT methods and RPA-based calculations of the complex optical permeability tensors of crystals and polycrystals [1] (UMass Lowell). Some DFT results were also used as inputs into MD simulations (NCSU). DFT methods are known to accurately predict structural and mechanical properties of materials but fail to correctly calculate energies of excited states and, therefore, the electronic and optical properties. Traditional one-particle 'beyond-DFT' methods (e.g., GW approximation [2]) are not free of inaccuracies in bandgap energy prediction. Therefore, the PI and his collaborator decided to develop and implement a principally new 'many-particle' approach to first-principles calculations.

3, Novel methods

Dr. Adil-Gerai Kussow (research faculty at UConn) shared his unfinished manuscript that contains a principally new theoretical physics framework, and also recommended to consult relevant literature, e.g., [3];

We also discussed a simple problem that can be used to test his method: excited states in noble gases (e.g., argon), for which excited state energies were predicted well using traditional methods. The steps in the new method are as follows:

1) A non-relativistic many-particle Hamiltonian is introduced;

2) Then, that Hamiltonian is expressed as a sum of two-particle Hamiltonians by means of a unitary transformation;

3) Many-electron wavefunctions are introduced and expressed as a linear combination of two-particle wavefunctions that are then expressed in one-particle wavefunctions;

4) The total energy of all electrons in the effective potential of the nuclei is found, Coulomb and exchange-correlation energies are added to it;

The latter step (4) requires computing multidimensional integrals in the real space and is the most computationally expensive in the whole scheme.

These perturbed two-particle wavefunctions are used in step (4) for the calculation of electron energies. [4].

There are several types of numerical methods involved in this project:

- Evaluation of multidimensional integrals (e.g., by Monte Carlo integration [5]);
- Integration in the complex plane;
- Combinatorics (was taken care of by the collaborator, who reduced all many-body problems to two-body and one-body problems);
- Linear algebra (standard numerical algorithms are appropriate);

5. Application of parallel computing to this problem

The problem is easy to implement on a parallel computer, because:

- Multiple threads are useful when computing interactions between valence electrons in many-electron molecules;
- Corrections to the wavefunctions using two-particle Green's functions can also be computed in parallel;

The number of threads depends on the total number of valence electrons in all atoms that are taken into account.

6. Benefits for Lincoln University

Although the level of physics is more appropriate for graduate students, undergraduates can be involved in some related work:

- Math majors can work on numerical evaluation of multidimensional integrals, combinatorics;
- Physics majors (hope, we get some) can also work on quantum mechanical computations;

- Chemistry majors, if there are any students interested in quantum chemistry.
- CS majors may help with the parallel implementation;

7. Work in progress

Implementation of the novel method on XSEDE parallel computer through the University of Delaware resource allocation will continue until August 2022. The progress was impeded by multiple competing research projects (NASA, AFRL, NSF, etc.).

8. Conclusions

This faculty development grant helped the PI to enhance his understanding of the Green's function methods used in the first-principles calculations of excited state energies and optical properties in simple molecules. The PI has also attended several webinars on the use of parallel programming environments, particularly those used by the XSEDE supercomputer.

References

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2. Michael Rohlfing Steven G. Louie, Electron-hole excitations and optical spectra from first principles Physical Review B, 62, 8, 15 Aug. 2000-II.
3. A. Baz', Ya. Zel'dovich, A. Perelomov, "Scattering, Reactions, and Decay in Nonrelativistic Quantum Mechanics," Moscow, 1966.
4. A.G. Kussow, Exact fermionic many-electron wave function derived from two-particle excitations: key to alternative first-principles methods, unpublished, 2021.
5. W.H. Press, S.A. Teukolsky, W.T. Vetterling, B.P. Flannery, 2007. "Numerical Recipes: The Art of Scientific Computing (3rd ed.)". New York: Cambridge University Press.