Chemistry Department, Indiana University

Research Review
Summer 2015

QWAIMD on a moving grid

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Acknowledgments

I would like to thank Prof. Iyengar for giving me the opportunity to work in his research group. His constant guidance and supervision were key to my work. I am also grateful to all the members of the group for all their help. Special thanks to Junjie Li for his patience in explaining the code and help in debugging. Finally I would like to thank the Department of Chemistry, the Graduate School and the Dean's Office for funding my stay here.

Introduction

The main objective of my research is to formulate and implement Quantum Wavepacket Ab Initio Molecular Dynamics (QWAIMD) on a moving grid. This entails extending the existing QWAIMD formalism theoretically to allow for a moving grid, making the requisite changes in the code accordingly and analyzing the results.

Formulation

I started with learning the relevant theory of QWAIMD. This is a hybrid quantum-classical approach to molecular dynamics. Certain parts of the system are treated using semi-classical ab initio molecular dynamics while others quantum mechanically so that the computationally taxing quantum dynamics calculations are performed only for the parts expected to manifest quantum phenomena. I learned about the systematic approximations made at each stage of the theory. Starting out with the time dependent Schrodinger equation, the mean field approximation (TDSCF) is used to "separate" the dynamics of the classical nuclei, electrons and the quantum nuclei. As the name suggests the interactions between different parts of the system are averaged out.

The dynamics of classical nuclei and electrons can be treated using a variety of well known ab initio dynamics techniques. I read through the ones that have been analyzed and tested in the QWAIMD formalism viz. Born-Oppenheimer molecular dynamics (BOMD) and atom-centered density matrix propagation (ADMP) with emphasis on the latter. ADMP is an exmple of extended Lagrangian approach to ab initio molecular dynamics. This introduced me to techniques like Born-Oppenheimer approxiamtion, Bohmian mechanics (used to extract semi-classical mechanics from quantum mechanics), Hellman-Feynman forces (and the corrective Pulay terms), velocity Verlet algorithm. I also got a glimpse into the vast electronic structure theory learning about the Hartree-Fock self consistent field theory (including McWeeny's density matrix approach) and a touch of density functional theory.

Computing the dynamics of quantum nuclei presents with the daunting task of integrating the TDSE. Study of quantum propagation introduced me to a rich array of computational techniques. QWAIMD samples the wavefunction on a grid of points and follows the split-operator approach for quantum propagation. The free propagator is approximated using density approximating functionals (DAFs) leading to a an banded, sparse and Toeplitz representation of the propagator. I also glanced over computational

improvements to the approach like the potential-adapted, time-dependent deterministic sampling technique (TDDS).

Let me highlight the motivation behind using a moving grid for sampling the wavepacket. Traditionally a fixed grid oriented along the donor-acceptor axis is used. For the cases where the quantum nucleus interacts with entities other than the donor and the acceptor or there is a significant change in the orientation of the donor acceptor axis during the course of motion, use of a moving grid becomes convenient if not obligatory to some extent. It is also computationally efficient to use a moving grid for the class of problems where the localized wavepacket translates over a significant distance.

The grid can be considered to be a set of delta basis functions to be used to expand the wavepacket. First consideration is determining the criterion for movement of the grid. As a simplistic starting point, the grid is centered at the wavepacket center and oriented along the donor-acceptor axis at every step of the simulation. This entails both rotation and translation of the grid.

Using a moving grid leads to modifications in dynamics of all three parts of the system. The wavepacket and potentials need to be transformed to the newly computed grid at every step. DAFs are used to approximate the transformation tensor in a computationally efficient manner. PES is smoothened by a Taylor series like expansion during transformation. Forces on the classical nuclei are modified because of the motion of the grid leading to Pulay like correction terms to the classical Hellman-Feynman approximation. While analyzing these additional terms a similarity to forces used in ADMP became apparent. I spent some time in formalizing this analogy.

Implementation and Analysis

After getting some idea of the changes needed to account for a moving grid, I moved on to the implementation part of the problem. First step was to read through the relevant parts of the existing QWAIMD code. Because of the huge size of the code and unfamiliarity with some parts of the theory, a systematic and careful analysis was required. Emphasis at this stage was on the code related to the calculation of the grid. Some code for implementing a moving grid was already in place. As a first step I made a few changes to the code for implementing a non-translating rotating grid of fixed size. Ignoring the requisite changes to the forces on classical nuclei, I ran some simulations to test the written code for grid movement and the modified wavepacket propagation.

I learned analyzing the large amount of data produced by the trajectory calculation (also became familiar with shell scripting in the process). After making sure that the grid is rotating as expected and counting out the result

of erroneous forces on classical nuclei, comparison were made of the results between fixed and rotating grid simulations. I tried working with different molecular systems looking for significant rotation of donor-acceptor axis. I also tried simulating with a pulsating grid and looked for differences between all the cases. Even with a fixed grid serious energy and momentum conservation problems were encountered. I read through the dynamics part of the code thoroughly to figure out the issue. Although there is some understanding of the underlying cause it has not been sorted out completely so far.

Future prospects

I intend to continue working on the problem and hope that I can make significant progress in the direction of completing the implementation. After fixing the angular momentum conservation issue, next step would be to implement the forces on classical nuclei. There could be scope for improvement in the theoretical formalism of forces as well.