

An Embarrassingly Parallel *ab initio* MD Method for Liquids

Fredrik Hedman¹ and Aatto Laaksonen²

¹ Paralleldatorcentrum (PDC),
Royal Institute of Technology, S-100 44 Stockholm, Sweden.
`hedman@pdc.kth.se`

² Department of Physical Chemistry, Arrhenius Laboratory,
Stockholm University, S-106 91 Stockholm, Sweden.
`aatto@tom.fos.su.se`

Abstract. A method to perform embarrassingly parallel *ab initio* molecular dynamics simulations of liquids on Born-Oppenheimer surfaces is described. It uses atomic energy gradient forces at an arbitrary level of quantum chemical methodology. The computational scheme is implemented with an MD program interfaced to a quantum chemistry package. Parallelization is done using the replicated data method.

Scaling results for up to 96 processors on an SP2 are presented. Results from simulations of liquid water at the *ab initio* SCF-MO Hartree-Fock level using single and double zeta basis function sets are compared with experimental radial distribution functions.

1 Introduction

Molecular dynamics (MD) computer simulations have over the last three decades become an important tool to study many-particle systems and nearly every possible aspect of condensed matter. The enabling factors in this development has been a combination of the growth in computer performance and capacity and more efficient simulation methods. With the arrival of massively parallel computer systems the raw computational capacity is abundant and this increased computing capacity can be used to improve the accuracy and reliability of molecular simulations.

Fundamentally there are three directions of development to follow: the time scales of the system, the size of the system and the interaction potentials of the system. In this communication we focus on a method that uses more realistic interaction potentials close to fundamental principles of molecular physics.

One such approach are so called polarizable interaction potentials and distributed multipoles [1]. With these models we are still in the domain of classical effective pair potentials, so even though the cost of calculating each interaction is greater, the simulation cost for a system containing N interaction sites is still of order $O(N \log N)$ to $O(N)$. By introducing electrons through quantum mechanical interactions between some or all particles in the simulation the accuracy of the simulation improves, but the computational cost will rise dramatically. The

increased computational demand will be dominated by the level of sophistication of the quantum model (Semi-empirical, Hartree-Fock, DFT, MP2, etc).

We present a general method to perform *ab initio* MD simulations of liquid systems with periodic boundary conditions by first discussing the inclusion of first principles force fields in MD (Section 2). Then we go on to describe an implementation strategy which is based on extensive code and program reuse (Section 3). Scaling results for an embarrassingly parallel implementation using replicated data, running on up to 96 processors on an IBM SP2, is discussed (Section 4). Finally, some results from simulations of liquid water at the *ab initio* SCF-MO Hartree-Fock level using single and double zeta basis function sets are compared with experimental radial distribution functions (Section 5). We conclude with a summary (Section 6).

2 Including First Principles Force Fields in MD

To advance the MD computer simulation methods to studies of chemical processes, presently used force fields must be replaced. This is simply because the present models cannot treat phenomena such as dissociation, electron transfer or excited states. Fundamental quantum mechanics must be introduced into the simulation methods to replace the simple empirical interaction models. Unfortunately, to solve the time-dependent Schrödinger equation for condensed systems of some reasonable size is still far beyond current computational capacities.

One possible strategy to a quantum mechanical MD method, in which forces are calculated as gradients of the variational energy expressions, can be constructed by *replacing* the classical intra- and inter- molecular force calculations in a classical MD program by the corresponding quantum mechanical force calculations. This approach has been successfully tested in [2].

We have used a modified version of the computer simulation program "McMoldyn" [3] as the classical starting point. "McMoldyn" is an implementation of the classical MD method based on the neighbor list (NL) technique and uses periodic boundary conditions with minimum image criteria. The classical pairwise force calculations was replaced with a quantum mechanical (QM) calculation through and interface to a quantum chemistry package. To continue with periodic boundary conditions, each central molecule in every NL is treated equivalently. For each time step and for each molecule in the simulation we get one QM "cluster" calculation with its current NL included and minimum image criteria applied. To ensure energy conservation, all QM calculations are carried out to the same accuracy. Thus for each time step we get the following algorithm:

1. The MD program generates input files for the quantum chemistry program. The coordinates of the molecules, currently kept in the neighbor lists, are used. The molecules in each neighbor list become "clusters", which are input into a QM calculation. With N molecules in the simulation cell, N quantum mechanical cluster calculations are carried out in each time step.
2. From each cluster calculation we extract the forces acting on the central atom in the cluster. After having looped through all N clusters and calculated the