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QS-DRDC Accelerated Molecular Dynamics

Version 1.0

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Contrat Number: W7701-6-4979

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Abstract

In this manual we present a brief description of the first version 1.0 of QS-DRDC Accelerated Molecular Dynamics code, the methodology behind this code, implementation, and installation. A description of keywords and preparation of input files as well as output files is presented.

1. Introduction:

Molecular dynamics (MD) is a form of computer simulation wherein atoms and molecules are allowed to interact for a period of time under known laws of physics, giving a view of the motion of the atoms. The term MD is used to describe the solution of the classical equations of motion (Newtonian's equation) for a set of atoms or molecules. Because molecular systems generally consist of a vast number of particles, it is impossible to find the properties of such complex systems analytically; MD simulation circumvents this problem by using numerical methods. It represents an interface between laboratory experiments and theory, and can be understood as a "virtual experiment". This was accomplished by Alder and Wainwright in 1957 and 1959, respectively. In this case, the particles move at constant velocity between perfectly elastic collisions, and it is possible to solve the dynamic problem without making any approximations, within the limits imposed by an accurate force field together with machine accuracy.

An accurate force field is an important element in the MD method, as it permits large systems to be studied at relatively little computational cost. However, current classical force field technology is not capable of describing chemical events involving bond breaking and forming. Another deficiency of current force fields is their failure to include polarization effects, although polarizable force fields have been introduced in the last few years. The technique known as *ab initio* molecular dynamics (AIMD) solves these problems by combining "on the fly" electronic structure calculations with finite temperature dynamics. Not surprisingly, AIMD simulations are substantially more expensive than calculations based on empirical force fields. However, recent advances in electronic structure theory as well as readily available high-speed computers have begun to render the AIMD approach a viable one for studying chemical processes in the condensed phase.

The most important element in an AIMD calculation is the representation of the electronic structure. Clearly, calculation of the exact ground-state electronic wavefunction is intractable, and approximations must be used. The electronic structure theory employed should be reasonably accurate yet not too computationally demanding. One formulation of the electronic structure problem that satisfies these criteria is density functional theory (DFT). DFT formulates the many-electron problem in terms of the electron density, $\rho(\vec{r})$, rather than the many-body wavefunction. Thus, in principle, the central quantity is a function of just three rather than of $3N$ variables, a fact that renders calculations based on DFT computationally tractable. The basic tenet of DFT is that the energy of a quantum many-body system can be expressed as a unique functional of its density. By minimizing the density functional over all densities that give rise to a particular number of electrons, one obtains the ground state density and energy for a given system. Unfortunately, the explicit and unique form of this functional is not known. However, in the orbital-based formulation of DFT by Kohn and Sham, reasonable approximations to the density functional have been developed. In the Kohn-Sham formulation, the energy is expressed in terms of a set of n occupied single-particle orbitals $\Psi_1(\vec{r})\dots\Psi_n(\vec{r})$ and the N nuclear positions, $\vec{R}_1, \dots, \vec{R}_N$, and takes the form;

$$E[\{\varphi\}, \{\vec{R}\}] = -\frac{1}{2} \sum_{i=1}^n \int dr \varphi_i^*(r) \nabla^2 \varphi_i(r) + \frac{1}{2} \int dr dr' \frac{\rho(\vec{r})\rho(\vec{r}')}{|r-r'|} + E_{xc}[\rho(\vec{r})] + \int dr V_{ext}(\vec{r}, \vec{R}_1, \dots, \vec{R}_N) \rho(\vec{r}) \quad (1.1)$$

where density $\rho(\vec{r})$ is related to the orbitals by

$$\rho(r) = \sum_{i=1}^n |\varphi_i(\vec{r})|^2 \quad (1.2)$$

and the orbitals are required to be mutually orthonormal,

$$\langle \varphi_i | \varphi_j \rangle = \delta_{ij} \quad (1.3)$$

In Eq. (1.1), V_{ext} represents the external potential due to the N nuclei and is given exactly by $V_{ext} = -\sum_{I=1}^N \frac{q_I}{|\vec{r} - \vec{R}_I|}$, where q_I is the charge on each nucleus. The first two terms in Eq. (1.1) are the electronic and Hartree energy terms, respectively. The functional $E_{xc}[\rho(\vec{r})]$ of the density, called the exchange-correlation functional, is unknown and must be approximated. For certain classes of systems, it has proved sufficient to approximate this functional by taking the exchange and correlation energies of a homogeneous electron gas and substituting for the constant density, n , the inhomogeneous density $\rho(\vec{r})$. This approximation, known as the *local density approximation* (LDA), has proved useful and reasonably accurate in many problems of interest in metallic and semiconductor solids. However, it fails, for example, in hydrogen-bonded systems, where spatial variations in the electron density are too rapidly varying to be described adequately by LDA. The most common approach in such cases is to extend the dependence of this functional to include the density $\rho(\vec{r})$ and its gradient $\nabla\rho(r)$: $E_{xc}[\rho(\vec{r}), \nabla\rho(\vec{r})]$. This approximation is known as the *generalized gradient approximation* (GGA) and has become a popular approach due to the recent development of improved functionals.

A possible strategy for combining electronic structure with molecular dynamics is the following: for a given set of initial nuclear positions $\vec{R}_1, \dots, \vec{R}_N$, minimize the energy functional in Eq. (1.1) to obtain the ground state density $\rho(\vec{r})$ and corresponding orbitals $\Psi_1(\vec{r}), \dots, \Psi_n(\vec{r})$. Given these quantities, the forces between the nuclei are given by the Hellman-Feynman theorem:

$$F_I = -\frac{\partial}{\partial R_I} E[\{\varphi^{(0)}\}, \{R\}] \quad (1.4)$$

The forces are then fed into a numerical integration procedure together with a set of initial velocities for the nuclei, and a step of molecular dynamics is carried out, yielding a new set of positions and velocities. At the new nuclear positions, the energy functional is minimized again and a new set of forces is obtained and used to perform another step of MD propagation. This procedure is repeated until an entire trajectory has been generated.

An important, developing area of MD methodology is the combination of the *ab initio* approach with empirical force fields. Such a combined scheme is expected to be of considerable utility in the treatment of large systems, in which chemical processes occur in a relatively localized region, e.g., at the active site of an enzyme or a chemical reaction in solution. In such systems, *ab initio* MD can be used to treat the chemically active region and a force field employed to describe the rest of the system. One of the difficult problems associated with a combined scheme is specifying how the electrons and nuclei in the *ab initio* region interact with the atoms in the force-field region. This is an especially challenging problem when it is necessary to "cut" bonds within a molecule, for example, in treating a reaction at the active site of an enzyme.

Ab initio force field is not limited to DFT calculations. Other electronic structure based force fields have also been implemented in AIMD applications, including semi-empirical quantum chemistry and tight-binding DFT. The efficiency for implementation is strongly dependent on the form of basis functions. An elegant alternative formulation of this implementation was proposed by Car and Parrinello using plane wave functions, in which, rather than minimizing the functional at each new nuclear configuration, a fictitious dynamics for the electronic orbitals is introduced, which allows them to follow the motion of the nuclei adiabatically. This dynamical procedure is constructed in such a way that if the orbitals are initially

chosen corresponding to the ground state density at the initial nuclear configuration, they will remain approximately the ground state as the nuclear configuration evolves in time. In the original formulation of the Car-Parrinello scheme, the orbitals are expanded in a plane wave basis.

Though AIMD simulations have been extensively employed to study the finite temperature behaviour of chemical systems at the atomic level, the use of this method requires the calculation of the electronic structure at each time step of the simulation and hence the time scales that can realistically be investigated with this method are limited to the sub-nanosecond regime. Unfortunately, the observation of chemical reactions, even those with modest barriers of 10 kcal/mol, may require an increase in these time scales by many orders of magnitude. The underlying reason for this is that although the reactive event itself may be quite rapid, a large amount of time is spent waiting for it to occur. These events are termed rare reactive events since in the context of the AIMD simulation the likelihood of their occurrence is minimal. To observe rare reactive events through AIMD simulation it is typically necessary to employ special sampling techniques that effectively decrease this waiting period such that these reactive states are accessible within the time scales of the simulation.

The umbrella sampling technique incorporates additional potential energy terms, called bias potentials, into the Hamiltonian to modify the potential energy surface (PES) such that the energetic barriers to chemical reactions are decreased. The rate of a chemical reaction is exponentially related to the activation energy, at least within transition state theory and acts of a metric of the accessibility of the associated reactive state. Hence the use of bias potentials that decrease activation energies may increase the accessibility of reactive states and allow for the observation of rare reactive events through AIMD simulation. Furthermore, bias potentials can be applied without a priori knowledge of the reaction, unlike many other sampling techniques, which is useful since such knowledge is quite often unavailable. Although, increasing

the temperature will have a similar effect of enhancing the accessibility of reactive states, the use of a bias potential provides an alternative approach that may be more selective in promoting specific processes.

Several bias potentials have been developed; however, few attempts have been made to incorporate aspects of the electronic structure into these expressions. Since chemical reactions are largely governed by changes in electronic structure, and this information is readily available in an AIMD simulation, it may be particularly advantageous to instead develop bias potentials based on electronic properties. One property of the electronic structure that changes in a consistent manner for a wide variety of chemical reactions is the difference in energies between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), the HOMO–LUMO gap. For many reactions involving the interaction of these two orbitals the value of the HOMO–LUMO gap is a minimum at, or near, the transition state. An innovative bias potential involving the smearing of orbital occupations around the Fermi level that incorporated this property of the HOMO–LUMO gap was recently proposed by VandeVondele and Rothlisberger. Although its performance in actual biased MD simulations was not reported, the bias potential was shown to significantly decrease activation energies along known reaction coordinates, suggesting its aptitude in accelerating the sampling of reactive states.

Following the bias proposed by VandeVondele and Rothlisberger, we present a bias potential that involves the addition of a constant portion of the HOMO–LUMO gap itself to the total potential energy of the system. Since the HOMO–LUMO gap is larger at the minima than it is at the transition states the activation energies for reactions leading out of these minima are decreased. We have also examined the behavior of this bias along predetermined reaction coordinates as well as through MD simulations. The results of these calculations have shown that this bias is useful in the study of rare chemical events. It should be noted that the dynamics resulting from a

biased MD simulation do not, in general, correspond to the true dynamics on the unbiased PES. For example, the relative rates of competing reactions are not preserved since the bias potential does not affect all transition state energies in an equivalent manner. Nonetheless the dynamics on the biased PES are useful in a qualitative sense by providing insight into possible reactive events, whereas on the unbiased PES none of these events would be observed due to time scale limitations.

2. Methodology

With the combination of HOMO and LUMO molecular orbital, bias potential energy E_{bias} is defined as:

$$E_{bias} = \int (\Psi_L + \Psi_H)^\dagger \hat{O} (\Psi_L - \Psi_H) d\tau \quad (1.5),$$

where \hat{O} is an operator for the bias potential, $\Psi_L(\vec{r} - \vec{R}, \vec{c})$ and $\Psi_H(\vec{r} - \vec{R}, \vec{c})$ are LUMO and HOMO molecular orbital as function of electron coordinates \vec{r} , nuclear coordinates \vec{R} and wave function coefficients $c_{i\alpha}$, respectively. In here, we use localized basis functions. With plane wave basis function, orbital are not functions as nuclear coordinates. Normally, constructing bias potential operator is quite arbitrary as long as it gives smooth curve with respect to reaction coordinates. For our purpose, we have tested HOMO and LUMO energy difference, excitation energy and Hartree-Fock operator with local Dirac exchange potential. They all give smooth curve with respect to reaction coordinates using localized and non-localized basis functions. The calculation of biased energy is quite simple but derivative calculation with respect to nuclear coordinates is really challenged since gradient of wave function coefficients has to be calculated. The wave function coefficients are optimized with respect to total energy. In Kohn-Sham or Hartree-Fock calculations, since the total energy is already optimized with respect to the orbital coefficients, it is not necessary to determine changes in these coefficients. But for biased energy, the derivatives of those

coefficients with respect to nuclear coordinates are clearly necessary. However, frozen or partially frozen orbital approximation can be considered in order to save computational cost. As following, discussions will be made within frozen orbital approximation at first. Then, general consideration without frozen orbital will be given.

Taking Kohn-Sham or Hartree-Fock Hamiltonian as bias potential operator in Eq.(1.5), we have bias potential energy as:

$$E_{bias} = \varepsilon_L - \varepsilon_H \quad (1.6),$$

where ε_L and ε_H are HOMO and LUMO orbital energies satisfied with Kohn-Sham or Hartree-Fock equation:

$$\hat{H}\Psi_i = \varepsilon_i\Psi_i \quad (1.7).$$

In the following, Kohn-Sham Hamiltonian is taken as an example in derivative calculations due to convenient consideration. It can be applied to Hartree-Fock Hamiltonian without any problem.

The derivative of the bias potential energy with respect to a nuclear perturbation in direction a (x, y, or z) of atom α may be written as:

$$E_{bias}^a = \varepsilon_L^a - \varepsilon_H^a \quad (1.8).$$

The derivatives of the orbital energies can be obtained from Kohn-Sham equation. Multiplying by Ψ_i and integrating give an expression for ε_i :

$$\langle \Psi_i | H_{KS} | \Psi_i \rangle = \langle \Psi_i | \frac{-\nabla^2}{2} - V_N + V_e + V_{xc} | \Psi_i \rangle = \varepsilon_i \langle \Psi_i | \Psi_i \rangle \quad (1.9),$$

where V_N is nuclear attractive potential, V_e electron Coulomb potential, and V_{xc} exchange-correlation potential. Differentiating and rearranging yields:

$$\varepsilon_i^a = \langle \Psi_i^a | H_{KS} - \varepsilon_i | \Psi_i \rangle + \langle \Psi_i | -V_N^a + V_e^a + V_{xc}^a | \Psi_i \rangle \quad (1.10)$$

in comparison with the derivatives of the total energy,

$$E_{tot}^a = 2 \sum_i^{o.c.c} n_i \langle \Psi_i^a | H_{KS} - \varepsilon_i | \Psi_i \rangle + \sum_i^{o.c.c} n_i \langle \Psi_i | -V_N^a | \Psi_i \rangle \quad (1.11).$$

For the total energy there is:

$$\frac{\delta E_{tot}}{\delta \bar{C}} \equiv 0 \quad (1.12).$$

Therefore, we have:

$$\Psi_i^a = \sum_{\alpha} C_{\alpha i} \chi_{\alpha}^a(\vec{r} - \vec{R}) \quad (1.13).$$

In E_{tot}^a , the first term is Pulay orbital correction and the last one Hellmann-Feynman force.

Within frozen orbital approximation, the derivatives of bias potential energy are:

$$E_{bias}^a = \varepsilon_L^a - \varepsilon_H^a = \langle \Psi_L^a | H_{KS} - \varepsilon_L | \Psi_L \rangle + \langle \Psi_L | -V_N^a + V_e^a + V_{xc}^a | \Psi_L \rangle - \langle \Psi_H^a | H_{KS} - \varepsilon_H | \Psi_H \rangle + \langle \Psi_H | -V_N^a + V_e^a + V_{xc}^a | \Psi_H \rangle \quad (1.14),$$

using localized basis functions. It is obvious that if plane wave basis function is taken into account, the derivatives of bias potential energy is

$$E_{bias}^a = -\int (\Psi_L + \Psi_H)^\dagger V_N^a (\Psi_L - \Psi_H) d\tau \quad (1.15),$$

in comparison with the force on the ions due to the bias potential, which is given by:

$$\frac{\partial V_{bias}}{\partial R} \propto \int dr \sum_{HOMO,LUMO} \frac{\partial}{\partial R} \frac{\delta f_i \Psi_i^* \Psi_i}{|\vec{r} - \vec{R}|} \quad (1.16),$$

shown in the paper of Joost Vande Vondele and Ursula Rothlisberger.

However, without frozen orbital approximation using plane wave basis functions, it becomes back to Eq.(1.14) where Ψ_i^a is

$$\Psi_i^a = \sum_{\alpha} [C_{\alpha i}^a \chi_{\alpha}(\vec{r} - \vec{R}) + C_{\alpha i}^a \chi_{\alpha}^a(\vec{r} - \vec{R})] \quad (1.17).$$

In here, $C_{\alpha i}^a(\vec{R})$ stand for the derivatives of wave function coefficients. To calculate them analytically, the auxiliary transformation matrices U^a are introduced following Pople's approach. The non-diagonal elements are:

$$U_{ij}^a = \frac{\langle \Psi_i | H_{KS}^a | \Psi_j \rangle - S_{ij}^a \epsilon_j}{\epsilon_j - \epsilon_i} \quad (1.18)$$

and diagonal ones:

$$U_{ii}^a = -\frac{1}{2} S_{ii}^a \quad (1.19),$$

where S_{ij}^a is derivative of overlap integrals in molecular orbital. Finally, we have:

$$C_{ai}^a = \sum_j U_{ij}^a C_{\alpha j} \quad (1.20).$$

Since H_{KS}^a is function of C^a , iteration procedure is necessary to obtain matrices U^a .

3. Implementation:

Data structures and Computational kernels.

In the practical implementation of accelerated *ab initio* molecular dynamics, mathematical symbols have to be translated into data structures of the computer language. Then, mathematical formulas are set into computer code using the data structures. The layout of the data structures should be such that optimal performance for the algorithms can be achieved. However, based on the nature of this method, *ab initio* electronic structure calculations are independent on computational kernel and data structures because they are standalone as external packages, which provide *ab initio* force field and biasing potential derivatives. Usually, *ab initio* electronic structure packages need license for any modification and implementation with commercial purpose. Keeping these in mind, we found that mixing language programming is the best strategy for the general implementation. In addition, since semi-empirical quantum chemistry has public domain, we generated our own semi-empirical module which directly provides electronic structure based force field and biasing potential. Therefore, a complete package was written using FORTRAN 90/95 modern scientific computer language. This package shares same data structures and computational kernel of the implementation of this method. The script language is used to calling computational kernel and external electronic structure package for *ab initio* force field together with biasing potential. Thus, we have generated two packages, one is a complete package with semi-empirical quantum chemistry force field and biasing potential and the other is just computational kernel which calls

external packages using Perl script language. The users should have their own Gaussian 98 or Gaussian 03 and have license to do modification.

The following variables are used to denote quantities that measure system site.

- N_{at} : number of atoms.
- N_p : number of projects.
- $r(3, N_{at})$: nuclear positions.
- $v(3, N_{at})$: nuclear velocities.
- $f(3, N_{at})$: nuclear forces.

The variables of electronic structure calculations are listed in the computational kernel and kernel data structures. The molecular dynamic computational kernel is constructed using the Verlet algorithm, which may be written

$$\begin{aligned}
 p_i(t + \frac{1}{2}\delta t) &= p_i(t) + \frac{1}{2}\delta t \cdot f_i(t) \\
 r_i(t + \delta t) &= r_i(t) + \delta t \frac{p_i(t + \frac{1}{2}\delta t)}{m_i} \\
 p_i(t + \delta t) &= p_i(t + \frac{1}{2}\delta t) + \frac{1}{2}\delta t \cdot f_i(t + \frac{1}{2}\delta t)
 \end{aligned}
 \tag{1.21},$$

where p_i is the momentum of the particle i , and the pseudo code of computational kernel looks like,

```

do step = 1, nstep
  p = p + 0.5*dt*f
  r = r + dt*p/m
  f = force(r)
  p = p + 0.5*dt*f
enddo

```

Fig. 1. pseudo code of the Verlet algorithm.

4. Installation:

To install QS-DRDC-AMD, basic UNIX or LINUX knowledge is required. The user should be acquainted with the tar, gzip, and ideally with the make command of the UNIX or LINUX environment.

QS-DRDC-AMD requires that the BLAS package is installed on the computer. This package can be retrieved from many public domain servers, for instance <http://math-atlas.sourceforge.net>, but if possible one should use an optimized BLAS package from the machine supplier

To install QS-DRDC-AMD, create a directory for VASP to reside in. We recommend using the directory

```
~/QS-DRDC-AMD
```

In this directory, copy package tar file from media to here and then type

```
tar -zxvf qs-drdc-amd.tgz
```

By typing list command, one can see three directories generated, which called as src, bin and example. Enter bin directory, type make command to create executable file, called qs-drdc-amd.x. Using this executable file, one can run examples in example directory, where one can find some input files.

5. Input file and key words:

To run a job, one needs to prepare input file. The main input file, which is read as the standard input (unit 5), contains all the physical data of the system and the parameters

of the simulation to be performed. This file is written in a special format called flexible data format (FDF). This format allows data to be given in any order, or to be omitted in favor of default values. Here we offer a glimpse of it through the following rules:

- The FDF syntax is a 'data label' followed by its value. Values that are not specified in the datafile are assigned a default value.
- FDF labels are case insensitive, and characters - _ . in a data label are ignored. Thus, LatticeConstant and lattice_constant represent the same label.
- All text following the \# character is taken as comment.
- Logical values can be specified as T, true, .true., yes, F, false, .false., no. Blank is also equivalent to true.
- Character strings should **not** be in apostrophes.
- Real values which represent a physical magnitude must be followed by its units.

There is example for ammonia molecules.

```
NameOfSystems      Ammonia
LabelOfSystem      NH3

NumberOfSpecies    2

TypeOfBasis        SEbasis

Structure          Molecule

ComputeMullikenCharge T

%block SpeciesNumberNameCharge
  1 N 7.0
  2 H 1.0
%endblock SpeciesNumberNameCharge

NumberOfAtoms      4
```

```

UnitsOfCoordinates   Ang

%block CoordinatesAndSpecies
  0.177578  0.194751 -0.171632 1
  0.829310 -0.106783 -0.864461 2
 -0.652175 -0.354903 -0.242966 2
  0.578790  0.064051  0.732603 2
%endblock CoordinatesAndSpecies

SpinPolarized       F

MixBeta             0.6

MolecularDynamics  T
MDTimeStep         2.0
InitMDTemp         300.
NumMDSteps         20000
BiasingPotential   T
MDAlpha            0.8

```

As following, the general key word description is given:

NameOfSystems:

A string of one or several words containing a descriptive name of the system (max. 150 characters).

Default value: blank

LabelOfSystem:

A word (max. 20 characters {without blanks}) containing a nickname of the system, used to name output files.

Default value: qs-drdc-amd

NumberOfSpecies:

Number of different atomic species in the simulation.

Default value: There is no default. You must supply this variable.

SpeciesNumberNameCharge:

data block: It specifies the different chemical species that are present, assigning them a number for further identification. QS-DRDC-AMD recognizes the different atoms by the given atomic number.

```
Default value: There is no default. You must supply this
                variable.
```

```
%block SpeciesNumberNameCharge
      1 N 7.0
      2 H 1.0
%endblock SpeciesNumberNameCharge
```

The first number in a line is the species number, it is followed by the atomic number, and then by the desired label. This label will be used to identify corresponding semi-empirical parameters.

NumberOfAtoms:

Integer: Number of atoms in the simulation.

```
Default value: There is no default. You must supply this
                variable.
```

UnitsOfCoordinates:

A string: define unit of atomic coordinates.

```
Default value: Ang (Angstrom).
```

CoordinatesAndSpecies:

data block: atomic coordinates and atomic species.

The reading is done this way:

```
From ia = 1 to natoms
  read: xa(ix,ia), isa(ia)
```

where $xa(ix,ia)$ is the coordinate of atom ia , and isa is the species index of atom ia .

For example, we have data block **CoordinatesAnd Specise** of an ammonia molecule:

```
%block CoordinatesAndSpecies
  0.177578  0.194751 -0.171632 1
  0.829310 -0.106783 -0.864461 2
 -0.652175 -0.354903 -0.242966 2
  0.578790  0.064051  0.732603 2
%endblock CoordinatesAndSpecies
```

SpinPolarized :

Logical variable: to define spin configuration.

Default value: F

MixBeta :

Real variable: for self-consistent mixing parameter.

Default value: 0.6

MDTimeStep:

real variable: molecular dynamic time step.

Default value: 1.0

InitMDTemp:

real variable: initial temperature.

Default value: 300

NumMDSteps:

integer variable: total molecular dynamic time.

Default value: 1

MDAlpha:

Real variable: biasing parameter.

Default value: 1.0

SemiEmpiricalModel:

A string variable: to define semi-empirical quantum chemistry model

Default value: am1

6. Output files:

1. qs-drdc-am.log: this is output file containing most info.
2. Velocity.xyz: this file contains particle velocity trajectory.
3. Coordinates.xyz: this file contains particle coordinate trajectory.
4. system.xyz: this file contains initial geometry of molecule.
5. energy.log: this file contains all info about energy.

7. References:

1. Fermi, E.; Pasta, J.; Ulam, S. *Los Alamos preprint* **1955**, LA-1940.
2. Fermi, E. *Collected Papers* **1965**, II, 978.
3. Alder, B. J.; Wainwright, T. E. *J. Chem. Phys.* **1957**, 26, 1208.
4. Alder, B. J.; Wainwright, T. E. *J. Chem. Phys.* **1959**, 31, 459.
5. Rahman, A. *Phys. Rev.* **1964**, 136A, 405.
6. Verlet, L. *Phys. Rev.* **1967**, 159, 98.
7. Car, R.; Parrinello, M. *Phys. Rev. Lett.* **1985**, 55, 2471-2474.
8. Galli, G.; Parrinello, M. *Computer Simulation in Materials Science* **1991**, 3, 283.
9. Laasonen, K.; Sprik, M.; Parrinello, M.; Car, R. *J. Chem. Phys.* **1993**, 99, 9081.
10. Sprik, M.; Hutter, J.; Parrinello, M. *J. Chem. Phys.* **1996**, 103, 1142.
11. Diraison, M.; Martyna, G. J.; Tuckerman, M. E. *J. Chem. Phys.* **1999**, 110, 000.

12. Tuckerman, M. E.; Laasonen, K.; Sprik, M.; Parrinello, M. *J. Phys. Condens. Matter* ,**1994**, *4*, A93.
13. Tuckerman, M. E.; Laasonen, K.; Sprik, M.; Parrinello, M. *J. Phys. Chem.* **1995**, *99*, 5749.
14. Tuckerman, M. E.; Laasonen, K.; Sprik, M.; Parrinello, M. *J. Chem. Phys.* **1995**, *103*, 150.
15. Marx, D.; Tuckerman, M. E.; Hutter, J.; Parrinello, M. *Nature* **1999**, *397*, 601.
16. Benoit, M.; Marx, D.; Parrinello, M. *Nature* **1998**, *392*, 258.
17. Sagnella, D. E.; Laasonen, K.; Klein, M. L. *Biophys. J.* **1996**, *71*, 1172.
18. M. Boero, M. P.; Terakura, K. *J. Am. Chem. Soc.* **1998**, *120*, 2746.
19. K. C. Hass, W. F. S. A. C.; Andreoni, W. *Science* **1998**, *282*, 265
20. Tuckerman, M. E.; Mundy, C. J.; Martyna, G. J. *Europhys. Lett.* **1999**, *45*, 149.
21. Swope, W. C.; Andersen, H. C.; Berens, P. H.; Wilson, K. R. *J. Chem. Phys.* **1982**, *76*, 637.
22. Kubo, R.; Toda, M.; Hashitsume, N. *Statistical Physics II*; Springer-Verlag: Berlin, 1978.
23. Berne, B. J.; Harp, G. D. *Adv. Chem. Phys.* **1970**, *17*, 63.
24. Andersen, H. C. *J. Chem. Phys.* **1980**, *72*, 2384.
25. Nosé, S.; Klein, M. *Mol. Phys.* **1983**, *50*, 1055.
26. Nosé, S. *J. Chem. Phys.* **1984**, *81*, 511.
27. Hoover, W. G. *Phys. Rev. A* **1985**, *31*, 1695.
28. Martyna, G. J.; Tuckerman, M. E.; Klein, M. L. *J. Chem. Phys.* **1992**, *97*, 2635.
29. Tuckerman, M. E.; Martyna, G. J.; Klein, M. L.; Berne, B. J. *J. Chem. Phys.* **1993**, *99*, 2796.
30. Tobias, D. J.; Martyna, G. J.; Klein, M. L. *J. Phys. Chem.* **1993**, *97*, 12959.

31. Martyna, G. J.; Tobias, D. J.; Klein, M. L. *J. Chem. Phys.* **1994**, *101*, 4177.
32. Tuckerman, M. E.; Martyna, G. J. *J. Chem. Phys.* **1999**, *110*, 3623.
33. Goldstein, H. *Classical Mechanics, 2nd edition*; Addison-Wesley: Reading, Mass., 1980.
34. Tuckerman, M.; Martyna, G. J.; Berne, B. J. *J. Chem. Phys.* **1992**, *97*, 1990.
35. Martyna, G. J.; Tuckerman, M.; Tobias, D.; Klein, M. *Mol. Phys.* **1996**, *87*, 1117.
36. Andersen, H. C. *J. Comput. Phys.* **1983**, *52*, 24.
37. Watanabe, M.; Karplus, M. *J. Chem. Phys.* **1993**, *99*, 18063.
38. Procacci, P.; Darden, T.; Marchi, M. *J. Phys. Chem.* **1996**, *100*, 10464.
39. Mizan, T. I.; Savage, P. E.; Ziff, R. M. *J. Phys. Chem.* **1994**, *98*, 13067.
40. Cui, S. T.; Cummings, P. T.; Cochran, H. D. *J. Chem. Phys.* **1996**, *104*, 255.
41. Komeiji, Y.; Uebayasi, M.; Takata, R.; Shimizu, A.; Itsukashi, K.; Taiji, M. *J. Comput. Chem.* **1997**, *18*, 1546.
42. Schlick, T.; Mandzuik, M. *Chem. Phys. Lett.* **1995**, *237*, 525.
43. Schlick, T.; Mandzuik, M.; Skeel, R. D.; Srinivas, K. *J. Comput. Phys.* **1998**, *140*, 1.
44. Tuckerman, M. E.; Parrinello, M. *J. Chem. Phys.* **1994**, *101*, 1302.
45. Williams, D. E. *Acta. Cryst. A* **1971**, *27*, 452.
46. Hockney, R.; Eastwood, J. *Computer Simulation using Particles*; McGraw-Hill: New York, 1981.
47. Pollock, E.; Glosi, J. *Comp. Phys. Comm.* **1996**, *95*, 93.
48. Essmann, U.; Perera, L.; Berkowitz, M. L.; Darden, T. A.; Lee, H. L.; Pedersen, L. G. *J. Chem. Phys.* **1995**, *103*, 8577.
49. Darden, T. A.; Toukmaji, A.; Pedersen, L. G. *J. Chim. Phys.* **1997**, *94*, 1346.
50. Greengard, L.; Rokhlin, V. *Physica Scripta* **1989**, *29A*, 139.

51. White, C.; Head-Gordon, M. *J. Chem. Phys.* **1994**, *101*, 6593.
52. Figueirido, F.; Zhou, R.; Levy, R.; Berne, B. *J. Chem. Phys.* **1997**, *106*, 9835.
53. Martyna, G. J.; Tuckerman, M. E. *J. Chem. Phys.* **1999**, *110*, 2810.
54. Jorgensen, W. L.; Chandrasekhar, J.; Madura, J. D.; Impey, R. W.; Klein, M. L. *J. Chem. Phys.* **1983**, *79*, 926.
55. Banks, J. L.; Kaminski, G. A.; Zhou, R. H.; Mainz, D. T.; Berne, B. J.; Friesner, R. A. *J. Chem. Phys.* **1999**, *110*, 1999.
56. Hohenberg, P.; Kohn, W. *Phys. Rev. B* **1964**, *136*, 864.
57. Kohn, W.; Sham, L. J. *Phys. Rev. A* **1965**, *140*, 1133.
58. Parr, R. G.; Yang, W. *Density Functional Theory of Atoms and Molecules*; Oxford University Press: New York, 1988.
59. Becke, A. *Phys. Rev. A* **1988**, *38*, 3098.
60. Lee, C.; Yang, W.; Parr, R. *Phys. Rev. B* **1988**, *37*, 785.
61. Perdew, J. P.; Wang, Y. *Phys. Rev. B* **1991**, *45*, 13244.
62. Perdew, J. P.; Burke, K.; Ernzerhof, M. *Phys. Rev. Lett.* **1996**, *77*, 3865.
63. Proynov, E. I.; Salahub, D. R. *Phys. Rev. B* **1994**, *249*, 7874.
64. Proynov, E. I.; Salahub, D. R. *Chem. Phys. Lett.* **1994**, *230*, 419.
65. Focher, P.; Chiarotti, G. L.; Bernasconi, M.; Tosatti, E.; Parrinello, M. *Europhys. Lett.* **1994**, *26*, 345.
66. Bernasconi, M.; Chiarotti, G. L.; Focher, P.; Scandolo, S.; Tosatti, E.; Parrinello, M. *J. Phys. Chem. Solids* **1995**, *56*, 501.
67. Mauri, F.; Galli, G. *Phys. Rev. B* **1994**, *50*, 4316.
68. Hutter, J.; Tuckerman, M. E.; Parrinello, M. *J. Chem. Phys.* **1995**, *102*, 859.
69. Hutter, J.; Parrinello, M.; Vogel, S. *J. Chem. Phys.* **1994**, *101*, 3862.
70. Silvestrelli, P. L.; Bernasconi, M.; Parrinello, M. *Chem. Phys. Lett.* **1997**, *277*, 478.
71. Benoit, M.; Bernasconi, M.; Parrinello, M. *Phys. Rev. Lett.* **1996**, *76*, 2934.

72. Bernasconi, M.; Silvestrelli, P. L.; Parrinello, M. *Phys. Rev. Lett.* **1998**, *81*, 1235.
73. Tuckerman, M. E.; von Roseninge, T.; Klein, M. L. *Mater. Res. Soc. Symp. Proc.* **1996**,
74. von Roseninge, T.; Tuckerman, M. E.; Klein, M. L. *Farad. Discuss.* **1997**, *106*, 273.
75. Tuckerman, M. E.; Klein, M. L. *Chem. Phys. Lett.* **1998**, *283*, 147.
76. Mei, H. S.; Bagchi, K.; Tuckerman, M. E.; Klein, M. L. *J. Phys. Chem.* **1999**, *104*,
77. Curioni, A.; Andreoni, W.; Hutter, J.; Schiffer, H.; Parrinello, M. *J. Am. Chem. Soc.* **1994**, *116*, 11251.
78. Curioni, A.; Sprik, M.; Andreoni, W.; Schiffer, H.; Hutter, J.; Parrinello, M. *J. Am. Chem. Soc.* **1997**, *119*, 7218.
79. Laasonen, K.; Klein, M. L. *J. Am. Chem. Soc.* **1994**, *116*, 11620. Laasonen, K.; Klein, M. L. *Mol. Phys.* **1996**, *88*, 135.
80. Meijer, E. J.; Sprik, M. *J. Am. Chem. Soc.* **1998**, *120*, 6345.
81. Mei, H. S.; Tuckerman, M. E.; Sagnella, D. E.; Klein, M. L. *J. Phys. Chem. B* **1998**, *102*, 10446.
82. Pavese, M.; Berard, D. R.; Voth, G. A. *Chem. Phys. Lett.* **1999**, *300*, 93.
83. Trout, B. L.; Parrinello, M. *Chem. Phys. Lett.* **1998**, *288*, 343.
84. Warshel, A.; Weiss, R. M. *J. Am. Chem. Soc.* **1980**, *102*, 6218.
85. Singh, U. C.; Kollman, P. A. *J. Comp. Chem.* **1986**, *7*, 718.
86. Field, M. J.; Bash, P. A.; Karplus, M. *J. Comp. Chem.* **1990**, *11*, 700.
87. Monard, G.; Loos, M.; They, V.; Baka, K.; Rivail, J.-L. *Int. J. Quant. Chem.* **1996**, *58*, 153.
88. Gao, J.; Amara, P.; Alhambra, C.; Field, M. J. *J. Phys. Chem. A* **1998**, *102*, 4714.

89. Feynman, R. P.; Hibbs, A. R. *Quantum Mechanics and Path Integrals*; McGraw-Hill: New York, 1965.
90. Feynman, R. P. *Statistical Mechanics: A set of lectures*; Benjamin Cummings: Reading, 1972.
91. Chandler, D.; Wolynes, P. G. *J. Chem. Phys.* **1981**, *74*, 4078.
92. Parrinello, M.; Rahman, A. *J. Chem. Phys.* **1984**, *80*, 860.
93. Hall, R. W.; Berne, B. J. *J. Chem. Phys.* **1984**, *860*, 3641.
94. Tuckerman, M. E.; Marx, D.; Klein, M. L.; Parrinello, M. *J. Chem. Phys.* **1997**, *104*, 5579.
95. Martyna, G. J.; Hughes, A.; Tuckerman, M. E. *J. Chem. Phys.* **1999**, *110*, 3275, Marx, D.; Parrinello, M. *J. Chem. Phys.* **1997**, *104*, 4077.
96. Marx, D.; Tuckerman, M. E.; Martyna, G. J. *Comp. Phys. Comm.* **1999**, *118*, 000.
97. Cao, J.; Voth, G. A. *J. Chem. Phys.* **1993**, *99*, 10070. Cao, J.; Voth, G. A. *J. Chem. Phys.* **1994**, *101*, 6157.

List of symbols/abbreviations/acronyms/initialisms

DND	Department of National Defence
MD	Molecular Dynamics
QS-DRDC-AMD	Q-Science-DRDC-Accelerated Molecular Dynamics
DFT	Density Functional Theory
AIMD	<i>Ab initio</i> Molecular Dynamics
$\rho(\mathbf{r})$	Electronic density
LDA	Local Density Approximation
PES	Potential Energy Surface
HOMO	Highest occupied molecular orbital
LUMO	Lowest unoccupied molecular orbital
GGA	generalized gradient approximation

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In this manual we present a brief description of the first version 1.0 of QS-DRDC Accelerated Molecular Dynamics code, the methodology behind this code, implementation, and installation. A description of keywords and preparation of input files as well as output files is presented.

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MD

Qs-DRDC AMD

DFT

HOMO

LUMO

PES

QS-DRDC Accelerated Molecular Dynamics

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Installation

FORTRAN 90/95

Structures

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