

Chapter 2

Ab Initio Molecular Dynamics

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Abstract

In this chapter, an introduction to ab initio molecular dynamics (AIMD) has been given. Many of the basic concepts, like the Hellman–Feynman forces, the difference between the Car–Parrinello molecular dynamics and AIMD, have been explained. Also a very versatile AIMD code, the CP2K, has been introduced. On the application, the emphasis was on the aqueous systems and chemical reactions. The biochemical applications have not been discussed in depth.

Key word: Ab initio molecular dynamics, Car–Parrinello method, Simulations of liquid water, Proton transfer

1. Background

The atoms and molecules are always in movement. Even at very low temperatures the atoms move due to the quantum motion, but by far the more important movement is the thermal motion. Because they move we should be able to model this movement. This can be done using empirical potentials and describing atoms as point particles (empirical molecular dynamics, EMD). The situation is more delicate when the system is described using quantum mechanics. In quantum mechanics both the electrons and nuclei are described using the Schrödinger equation:

$$i\hbar \frac{\partial \Psi(r_i, R_I, t)}{\partial t} = H \Psi(r_i, R_I, t), \quad (1)$$

$$H = -\sum_I \frac{\hbar^2}{2M_I} \nabla_I^2 + H_e, \quad (2)$$

$$H_e = -\sum_i \frac{\hbar^2}{2m_e} \nabla_i^2 + \sum_{i < j} \frac{e^2}{|r_i - r_j|} - \sum_{i, I} \frac{e^2 Z_I}{|r_i - R_I|} + \sum_{I < J} \frac{e^2 Z_I Z_J}{|R_I - R_J|},$$

where R_I is atomic position, Z_I is atomic charge, M_I is atomic mass, r_i is electronic position, and m_e is electronic mass.

It is rather delicate to extract the classical Newtonian dynamics from the Schrödinger equation. An interested reader can find the details from a review by Marx and Hutter (1). In the Ehrenfest molecular dynamics the electronic excitations can be taken into account in the mean-field approximation. Even the simplest version where only the ground state wave function is included, this approach involves solution of the time-dependent Schrödinger equation. This approach has not been used much, but it can be implemented rather efficiently (2):

$$M_I \frac{d^2 R_I(t)}{dt^2} = -\nabla_I \langle \Psi_0 | H_e | \Psi_0 \rangle, \quad (3)$$

$$i\hbar \frac{\partial |\Psi_0\rangle}{\partial t} = H_e |\Psi_0\rangle. \quad (4)$$

A simpler approach where only the ground state wave function is included and the wave function is assumed to be always at the minimum is called the Born–Oppenheimer molecular dynamics (BOMD). This is the most commonly used version of ab initio molecular dynamics (AIMD):

$$M_I \frac{d^2 R_I(t)}{dt^2} = -\nabla_I \min_{\Psi} \langle \Psi_0 | H_e | \Psi_0 \rangle, \quad (5)$$

$$H_e |\Psi_0\rangle = E_0 |\Psi_0\rangle. \quad (6)$$

Note that H_e depends on the atomic positions.

The next step is to solve the electronic Schrödinger equation. In the general case this is not possible, and some approximations are needed. These methods are discussed more in the chapter by Johansson, Kaila, and Sundholm. In AIMD we are interested in single-determinant methods like Hartree–Fock (HF) or density functional theory (DFT) where the many-electron wave function can be written as $\Psi_0 = \det |\psi_1, \psi_2, \dots, \psi_N|$ with some orthonormal single-particle orbitals; $\langle \psi_i | \psi_j \rangle = \delta_{ij}$. Even with approximate methods (DFT or HF), the computational cost of AIMD is very high. One needs to do a medium size quantum chemical calculation at every molecular dynamics time step. This limits significantly the size of the system that can be studied.

There are several publications of AIMD explaining the computational and theoretical details, but they cannot be reviewed here. I recommend the review (1) which gives a relatively complete view of the field until 2000 and a book by the same authors (3). Also the lectures in the CECAM tutorial of CP2K give up to date information on AIMD (4). Additional sources of information are the www pages of the major AIMD codes (5, 6). For example, the CPMD www page has a rather long list of publications in this field. In this chapter, I take a more practical view and explain some basics of the AIMD and motivate its usefulness.

The AIMD can be solved with two main methods, the Car–Parrinello method and using directly the Born–Oppenheimer equation (Eq. 5). The drawback of Eq. 5 is that the wave function has to be optimized at every time step.

1.1. Forces

The force acting on atoms can be computed from the term

$$F_I = -\nabla_I \min_{\Psi} \langle \Psi_0 | H_e | \Psi_0 \rangle. \quad (7)$$

If the wave function does not have explicit atomic position dependence the forces can be computed from a simpler equation proposed by Hellman and Feynman,

$$F_I^{HF} = -\min_{\Psi} \langle \Psi_0 | \nabla_I H_e | \Psi_0 \rangle. \quad (8)$$

In a more general case the derivatives of the wave function ($\nabla_I | \Psi_0 \rangle \neq 0$) have to be taken into account which complicates the calculations. These are called the Pulay corrections (or Pulay forces).

2. Car–Parrinello Method

The Car–Parrinello (CP) method (or CPMD) is based on an elegant idea of adiabaticity. The electrons are much lighter than the atoms, and thus they should follow (adiabatically) the atoms. This means that the explicit wave function optimization is not necessary. On the other hand, the orthonormality constraint of the single-particle orbitals has to be maintained. The orthonormality can be preserved using the method of Lagrange multipliers. Constraint terms ($\mathcal{G}_{ij} = \langle \psi_i | \psi_j \rangle - \delta_{ij} = 0$) with Lagrange multipliers (Λ_{ij}) can be added to the energy

$$\sum_{ij} \Lambda_{ij} (\langle \psi_i | \psi_j \rangle - \delta_{ij}). \quad (9)$$

During the dynamics the constraints $\mathcal{G}_{ij} = 0$ have to be kept, and this defines the Lagrange multipliers. Computationally this orthogonalization is one of the most expensive parts of the code. It scales as $N_e^2 N_{\text{basis}}$, where the N_e is the number of electrons and N_{basis} is the number of basis functions. The same Lagrange multiplier technique is used to keep the bond constraints in empirical MD.

The CPMD consists, of two dynamical equations, one for the nuclei and another for the electrons:

$$M_I \frac{d^2 R_I(t)}{dt^2} = -\nabla_I [\langle \Psi_0 | H_e | \Psi_0 \rangle + \sum_{ij} \Lambda_{ij} (\langle \psi_i | \psi_j \rangle - \delta_{ij})], \quad (10)$$

$$\mu \frac{d^2 \psi_i(t)}{dt^2} = -\frac{\partial}{\partial \psi_i} [\langle \Psi_0 | H_e | \Psi_0 \rangle + \sum_{ij} \Lambda_{ij} (\langle \psi_i | \psi_j \rangle - \delta_{ij})]. \quad (11)$$

The time evolution of both $R(t)$ and $\psi(t)$ can be solved from these equations. Note that Eq. 11 does not correspond to the true dynamics of the wave function which is described by the time-dependent Schrödinger equation. This is a fictitious dynamics that allows the electrons to follow the nuclei.

There is an interesting consequence of the Pulay forces in the Car–Parrinello dynamics. If the basis set depends on the atomic positions, also the overlap matrix will depend on them and the constraint term will have position dependence (1):

$$-\nabla_I \langle \psi_i | \psi_j \rangle \neq 0. \quad (12)$$

This term is missing from the publications since CPMD was originally developed for using the plane wave basis which does not depend on the atomic positions. Inclusion of this term will complicate the CP calculations using localized basis functions significantly, and BOMD (see Subheading 3) is more suitable when, for example, Gaussians are used as basis.

The CP method contains only one free parameter, the electron mass parameter μ . Due to the fictitious dynamics, μ does not need to be the electron mass. For sensible results, the starting wave function has to be well converged and the mass parameter much lighter than the lightest atom of the system (usually hydrogen or deuterium). The CPMD works well if the system has a stable electronic structure. This in practice means a large HOMO–LUMO gap (or band gap), which is the case with most chemically stable molecules.

The strength of the CPMD approach is that the wave function does not need to be optimized during the dynamics. The main drawback is that the (fictitious) electron dynamics is much faster than the nuclear motion, and a smaller time step for integration of the CPMD equations is needed. This time step depends on the mass parameter μ . For hydrogen-containing systems, reasonable values are $\mu = 300m_e$ and $\Delta t = 0.1$ fs. If one replaces the hydrogen with deuterium, the mass and time step can be increased slightly. Still, this time step is an order of magnitude smaller than in empirical MD. Thus, there is a prize to pay for neglecting the wave function optimization. Another minor drawback is that the movement of the reasonably massive electrons slows down the atomic motion. (A similar effect has been seen in the Ehrenfest dynamics implementation in (2).) This will, for example, cause a red shift of the hydrogen vibration frequencies.

On the other hand, CPMD will produce very stable trajectories, and often, 10^6 CPMD steps can be run with a very small drift in energy (1, 4).

3. Born–Oppenheimer Dynamics

AIMD can be done using Eq. 5 directly. The efficiency of this approach depends critically on how effectively the new wave function can be solved. In standard quantum chemical calculations the wave function solution takes tens of iterations, but the MD approach has one advantage. The wave functions from the few previous time steps can be utilized to make an excellent guess for the new wave function. The time step in BOMD is limited by the atomic dynamics and is similar to the time step in EMD, 1–2 fs. Thus, if the number of the wave function optimization steps can be pushed down to ca. 10, BOMD is computationally comparable to CPMD. With the latest algorithms, this is the case.

The BOMD trajectories are sensitive to the wave function convergence criterion, and good convergence is needed to achieve the same stability as in CPMD. Convergence (the largest element of the wave function gradient) of the order of 10^{-6} is needed. A good presentation of the stability of BOMD can be found in Hutter’s lectures in Ref. (4).

4. Quantum Chemistry

Besides dynamics, it is essential to choose the quantum chemical method to treat the electrons. Many quantum chemical codes like Gaussian (7) or Turbomole have the possibility to do AIMD, but they are not much used (they are quite slow). Usually AIMD is done with programs that have been designed for it. Such codes are CPMD, CP2K, NWChem, and to some extent VASP and CASTEP. The special AIMD codes do not provide many quantum chemical methods. By far the most used method is DFT using the generalized gradient approximation (GGA) (1). Also hybrid functionals, like B3LYP, can be used (8, 9), but they are computationally much more expensive. Very recently there has been improvement of the efficiency of the hybrid methods (10). The weak van der Waals interactions are not included in the GGA or hybrid functionals, but they can be added empirically to the calculations (11–13).

5. The Power of AIMD

AIMD calculations, are very expensive but they have one great advantage over the empirical methods—the electrons are included and thus the chemical bonds can break and form. The “force field” is also fully polarizable. Simply the used quantum chemical method sets the limits

of accuracy of the AIMD method. The numerical approximations like the basis set and pseudopotentials can be made quite small. Also the modern AIMD packages include most of the tools of empirical MD. These include the temperature and pressure control, and free energy calculations with different type of constraints. The latest AIMD codes can do similar simulations as empirical codes, but the system sizes and time scales are much smaller. This is of course a serious limitation in biochemical applications, and AIMD has not been much used in biochemistry. This does not mean that AIMD and especially QM/MM AIMD cannot be applied to biochemical problems. Only the number of suitable problems is rather limited. Also the state-of-the-art AIMD calculations are not easy to perform.

6. Practical AIMD Calculations

There are several computer codes that are designed to do AIMD. These include CPMD (5), CP2K (6), NWChem (14), and many others. Many of these packages are free, but they are not easy to install or use. The author of this chapter has long experience of using the CPMD and CP2K codes, and some comments of the usage of these codes are given below. AIMD simulations are very CPU time-consuming and very efficient parallel computers are needed. Naturally some test calculations can be done using a single PC, but for anything more serious, a supercomputer is needed. It is also important that the computer has fast communication between the processors. In this chapter I cannot go to the details of the code installations. For example, the latest version of CP2K can be downloaded from the Web. In the package, there are instructions for several computer architectures. The presentation of Guidon in Ref. (4) contains a lot of advice for installing CP2K, but very likely you will need also the help of the computer administrator.

For practical calculations one needs to worry about several parameters. These include the size of the system, simulation time, temperature, time step, quantum chemical model, basis set, and pseudopotentials. If the CPMD method is used also the effective electron mass has to be set. Of these the system size has to be set by the user. If aqueous systems are studied, the typical system size is ca. 100 waters with CPMD and up to 250 waters with CP2K. The accessible time scale is up to a few hundred picoseconds. Very often the simulations done are much shorter than 100 ps, but in my experience, reasonable equilibration requires usually around 25 ps. Often one needs to push the AIMD simulations as long as possible. Other solvents than water are harder to study since they contain more electrons. Systems like ionic liquids have been studied, but the system sizes and simulation times are very limited (15). In biochemistry several processes are much slower than this.

In some cases, constrained molecular dynamics can be used to study slow processes, but clearly, many biochemical problems are not accessible with AIMD.

The simulation temperature is often 300 K, but the temperature should be set to a bit higher, around 350 K to compensate for slow diffusion of water. The time step of a hydrogen- or deuterium-containing system in CPMD is 0.1–0.15 fs and in BOMD ca. 1 fs. As said earlier, the electrons are usually treated with DFT-GGA and the most used models are PBE or BLYP. I would recommend using the empirical van der Waals corrections in all calculations.

The basis set and pseudopotential combination is somewhat tricky. Some of the AIMD codes (CPMD, VASP, NWChem) use plane waves as the basis set, and they are very sensitive to the pseudopotentials. To keep the number of basis functions reasonably small, smooth pseudopotentials have to be used. For a nonexpert, the available pseudopotentials should be used, but care of their smoothness should be taken. In the CPMD package, the Troulier–Martins type pseudopotentials can be used. In VASP the PAW pseudopotentials are smooth and mostly reliable. The ultrasoft pseudopotentials proposed by Vanderbilt produce very smooth orbitals, and thus a low cutoff can be used, but the libraries of these pseudopotentials are not very complete.

The CP2K code uses Gaussians as basis. In the case of a Gaussian basis, the smoothness of the pseudopotentials is not an essential requirement, and CP2K has a rather complete pseudopotential library by Goedecker, Teter, and Hutter (16). Also all-electron calculations can be made.

Most of the used AIMD codes have a rather tricky interface. One of the most powerful AIMD codes, the CP2K, has a particularly complex interface, and the CP2K package does not have input examples. The presentations in the CP2K tutorial (4) are of some help, but unfortunately, the actual input examples are not included in the tutorial. This is annoying for someone who would like to do simple CP2K calculations, but the reason for this is that the CP2K is a complex code and the user should understand the input file, not just copy it from somewhere. To lower the barrier to use CP2K, I have included a simple example of 32 water molecules at the end of this chapter.

6.1. Equilibration

Because the AIMD time scale is quite short, a lot of care has to be paid in the system equilibration. If similar empirical MD can be done, it would work as good equilibration. This is a bit dangerous since then the equilibration is biased by the EMD force field and in short simulations, AIMD and EMD can seemingly agree very well. If EMD is not available (or it is not wanted to be used), a rather careful local optimization is needed before AIMD simulations. In any case, one needs to remember that molecular equilibration is a rather slow process compared to the AIMD time scale.

7. AIMD of Water

Liquid water has been the standard test for AIMD (17, 18). Naturally if AIMD (or more precisely the used DFT–GGA approach) fails to produce water properties correctly, it is not very useful for biochemical applications. The PBE or BLYP description of water is not perfect. The O–O pair correlation function is a bit too structured, and the diffusion coefficient is too small by a factor of 0.5. These results are somewhat worrying, and there have been several attempts to correct the DFT-GGA behavior (8, 9, 13). On the other hand, AIMD is the most reliable description of water when chemical reactions or strong solvation effects are considered. AIMD should be used for difficult cases like proton transfer reactions or chemical reactions in water.

8. AIMD of Reactions

In chemistry the chemical reactions are often of central importance. AIMD offers an excellent tool to study them. Unfortunately very seldom, the reactions are fast enough to happen in the AIMD (or even empirical MD) time scale. And even when they are fast enough several, events are needed to have a statistically meaningful description of the reaction. One important exception is the proton diffusion, which happens on the picosecond time scale and is accessible with AIMD. The proton diffusion has been studied in water (19), in a simple ion channel (20), ammonia (21) and water-methanol mixture (22). Also several other reactions can be studied with direct AIMD (there are a few examples in Ref. (1)).

With most reactions some method is needed to force the reaction to happen. In traditional quantum chemistry various transition-state search algorithms are used, but such approach is not useful in dynamical systems where the system is not in a local minimum. We need some biased dynamics, and the simplest method is to use a constraint to force the reaction to happen. The free energy of the reaction can be calculated by integrating the constraint force, F_g (g denoting some value of the constraint),

$$\Delta A = \int_{g_0}^{g_1} \langle F_g \rangle_T dg, \quad (13)$$

where $\langle F_g \rangle_T$ means the average at temperature T . Also normal thermodynamic integration can be done.

The simplest constraint is to fix the distance (or angle, or torsional angle) between two atoms, but many of the codes offer relatively complex choices of constraints. One can, for example, use

the coordination numbers as constraints. The calculation of the free energy differences requires quite a lot of computer time since to integrate the force several constraint values are needed, and due to the molecular collisions, the instantaneous constraint forces are very noisy and reasonable averaging has to be done at each constraint value. Simulations of the order of 10 ps are needed for converged results for each constraint value (23–25).

It is useful to check if similar barriers are achieved when the reaction is studied in both ways. If the reaction $A + B \rightarrow C$ is followed to some point, for example, to the transition state C^\ddagger , the calculations can be reversed, and when ended to the original state, the same energy barrier should be achieved. In practice there is always some hysteresis, and this path reverse test gives some idea of the size of the hysteresis.

More sophisticated biased simulations can be done using different algorithms including metadynamics. This is a very interesting field, and for more details, I refer to the CECAM CP2K Tutorial (4) and the presentations by Iannuzzi.

To summarize, the reaction calculations are probably the most important AIMD calculations. They are not as difficult as they look, but some toy projects should be done to learn how these calculations work. Research projects are usually so demanding that very little experimentation can be done. Whatever constraint or method one is using, the thermal collisions will cause large fluctuations to the constraint, and long averaging is needed. One should be prepared to do a total of 100–200 ps AIMD simulations. The only positive thing is that many of these calculations can be run simultaneously.

9. AIMD in Biochemistry

Biochemical applications of AIMD are not very common due to the slowness of the biochemical processes. Among the pioneers in this field are Ursula Röthlisberger (26, 27) and Paolo Carloni, but recently, of course many other groups have entered this field. In biochemical applications it is almost impossible to study the relevant system fully with *ab initio* methods, thus, the QM/MM modeling has become popular. There are a few chapters on QM/MM methods and applications in this book, so here I do not go to details of this type of modeling. It is still useful to mention that in most of the QM/MM calculations, the quantum atoms do not follow any dynamics. Thus, the developed AIMD-QM/MM methods are very attractive (some examples are given in the lecture by Kuo in Ref. (4)). In those methods the whole system, both the QM and MM parts, can move simultaneously. The QM part will determine the computational cost of the calculations, and its size should be small.

Unfortunately, the QM/MM calculations are rather complicated since one needs to understand/model the QM, MM parts, and the boundary between them. I do not have experience of AIMD-QM/MM calculations, so it is safer that I do not go into details. This field is in rapid development the algorithms become faster and the programs easier to use. Especially the latter is important for a non-expert user.

10. Exotic AIMD

I want to mention a couple of less common AIMD methods. The excited state dynamics have interesting applications in biochemistry, but the path integral method will probably have less biochemical applications.

10.1. Quantum Motion of Nuclei: Path Integral Ab Initio Molecular Dynamics

In the beginning, the Born–Oppenheimer approximation was used and the atoms were assumed as point particles. This is not necessary also the nuclear quantum motion can be modeled using the path integral molecular dynamics (PIMD) technique. The relevant equations are rather complex, and the details can be found in Refs. (1, 28). The PIMD has been implemented in CPMD and CP2K. The PIMD treatment is very interesting in the case of frustrated hydrogens, like in CH_5^+ or protons in water (29). Again the calculations are rather time-consuming, but new phenomena can be modelled.

10.2. Excited States

The static calculations of excited states are now quite routine. Most of the quantum chemical codes have routines to estimate the excited states. The time-dependent DFT (TD-DFT) is a very popular method and the computations are quite easy, but the results are not always very reliable. On the other hand, the molecular dynamics of molecules at excited states is not very developed, but it is an interesting direction for modeling. In Ref. (1), some basics of the excited state dynamics are described. R  thlisberger’s group has been active in this field, for one of their recent articles see Ref. (30). The methods capable of modelling excited states open possibilities for studying the very important photochemical reactions in biochemistry.

11. AIMD Has To Be Used: In Some Cases

I hope I have not been too pessimistic of the possibilities of AIMD in biochemistry. In my opinion it is a very valuable method for studying difficult topics like metal centers in proteins (31), chemical reactions in active sites, proton transfer reactions, properties of

excited states, etc. In my view any molecular modeling of proteins or biochemical systems is difficult since the time scales of these systems are long. In every case the system one wants to model has to be prepared carefully to be able to get meaningful results. Compared to EMD, the size and time limitations of AIMD are greater, but AIMD can solve problems EMD cannot.

The question is not whether one likes or does not like AIMD (or more generally quantum chemical methods) but that in some cases the QM methods have to be used. The information of atomic positions (and velocities) is not always enough, one also needs to know how the electrons behave.

12. Appendix: An Example Input for CP2K

Here is a simple input example for 32 water molecules. The POTENTIAL and BASIS_SET can be found from the CP2K package in the directory cp2k/test/QS. In this directory there are also a lot of test inputs that are useful when new types of runs are planned. A word of warning: They cannot be used as they are but often they complement the manual. A very similar input can be found in the file cp2k/tests/QS/benchmark/H2O-32.inp. (See the actual coordinates from this file).

```
&GLOBAL
  PREFERRED_FFT_LIBRARY FFTSG
  PROJECT w32-test
  RUN_TYPE MD
  PRINT_LEVEL LOW
&END GLOBAL

&MOTION
  &MD
    ENSEMBLE NVT
    STEPS 10000
    TIMESTEP 1.0
    &THERMOSTAT
      TYPE NOSE
      &NOSE
        TIMECON 310.0
      &END NOSE
    &END THERMOSTAT
    TEMPERATURE 348.15
  &END MD
&END MOTION
```

```
&EXT_RESTART
```

```
# EXTERNAL_FILE w32-test-1.restart # exist only after the first run
&END
```

```
&FORCE_EVAL
```

```
  METHOD Quickstep
```

```
  &DFT
```

```
    BASIS_SET_FILE_NAME ../cp2k_lib/BASIS_SET
```

```
    POTENTIAL_FILE_NAME ../cp2k_lib/POTENTIAL
```

```
  &MGRID
```

```
    CUTOFF 280
```

```
  &END MGRID
```

```
  &QS
```

```
    EPS_DEFAULT 1.0E-12
```

```
    EXTRAPOLATION ASPC
```

```
    EXTRAPOLATION_ORDER 3
```

```
  &END QS
```

```
  &SCF
```

```
    SCF_GUESS ATOMIC # for first time, next run SCF_GUESS RESTART
```

```
    EPS_SCF 0.4E-6 # this is important max is 1E-6
```

```
    MAX_SCF 25
```

```
  &OUTER_SCF
```

```
    EPS_SCF 1.0E-6
```

```
    MAX_SCF 2
```

```
  &END
```

```
  &OT
```

```
    MINIMIZER DIIS
```

```
    PRECONDITIONER FULL_ALL
```

```
    ENERGY_GAP 0.05
```

```
  &END
```

```
  &END SCF
```

```
  &XC
```

```
    &XC_FUNCTIONAL BLYP
```

```
  &END XC_FUNCTIONAL
```

```
  &END XC
```

```
&END DFT
```

```
&SUBSYS
```

```
  &CELL
```

```
    ABC 9.865 9.865 9.865
```

```
  &END CELL
```

```
  &COORD
```

```

O      2.280398      9.146539      5.088696
O      1.251703      2.406261      7.769908
O      1.596302      6.920128      0.656695
O      2.957518      3.771868      1.877387
. . . . find coordinates from cp2k/tests/QS/benchmark/H2O-32.inp
H      1.762019      9.820429      5.528454
H      3.095987      9.107088      5.588186
H      0.554129      2.982634      8.082024
H      1.771257      2.954779      7.182181
H      2.112148      6.126321      0.798136
H      1.776389      7.463264      1.424030
. . . .
&END COORD

&KIND O
  BASIS_SET TZVP-GTH
  POTENTIAL GTH-BLYP-q6
&END KIND

&KIND H

  BASIS_SET TZVP-GTH
  POTENTIAL GTH-BLYP-q1
  MASS 2.0000
&END KIND

&END SUBSYS
&END FORCE_EVAL

```

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