

# A Guide for the Practical Work

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**Abstract.** This document is a short guide for the practical work in the [2023 Molecular Modeling course](#). It details the goals and procedures for TP3, TP4, and TP5.

## 1 Introduction

Practical works TP3, TP4, and TP5 aim to help the students develop basic coding skills for molecular modeling. This document discusses the theory that will be employed. We aim to write, test, and apply a Python program to run molecular dynamics on a model potential energy surface (PES).

This will be accomplished through three parts:

- In the first part (TP3), we will implement a code to compute the adiabatic Spin-Boson PES discussed in masterclass CM3.
- In the second part (TP4), we will implement a code to run molecular dynamics based on the Velocity Verlet algorithm studied in masterclass CM1.
- Finally, in the third part (TP5), we will implement the Andersen thermostat introduced in masterclass SM1.

## 2 PES modeling (TP3)

The adiabatic Spin-Boson model<sup>1</sup> implements an  $N$ -dimensional pair of adiabatic potential energy surfaces. The ground-state ( $i = 1$ ) and excited-state ( $i = 2$ ) potential energies are

$$E_i = \frac{1}{2} \sum_{j=1}^N M_j \omega_j^2 R_j^2 + (-1)^i [\eta^2 + \nu_0^2]^{1/2} \quad (i=1,2) \quad (1)$$

where

$$\eta = \left( \sum_{j=1}^N g_j R_j + \varepsilon_0 \right) \quad (2)$$

In these equations, the nuclear coordinates are  $\mathbf{R} = (R_1, R_2, \dots, R_N)$ . The Spin-Boson model is characterized by several parameters  $\varepsilon_0$ ,  $M_i$ ,  $\omega_i$ ,  $g_i$ , and  $\nu_0$ . Their values are discussed later.

The potential energy gradient of the two adiabatic states is

$$\frac{\partial E_i}{\partial R_k} = M_k \omega_k^2 R_k + (-1)^i g_k \left[ \frac{\eta}{[\eta^2 + \nu_0^2]^{1/2}} \right] \quad (i=1,2; \quad k=1 \dots N) \quad (3)$$

**Task 1.** Implement a code to compute the adiabatic Spin-Boson model's energy and the energy gradient for the lowest state ( $i = 1$ ) in one dimension ( $N = 1$ ).

**Task 2.** Use your code to play with the model parameters. What is the effect of each one? What does the PES look like when you change them? And about the energy gradient?

**Tip:** Work in [Hartree atomic units](#).

Figure 1 illustrates the 1-D adiabatic Spin-Boson model with the parameters in Table 1. The ground state is a double well separated by an energy barrier. This model will be the basis for our next TP.

**Task 3.** Determine approximately ( $R_1$ ,  $R_2$ ) for the two minima.

**Tip.** You can find the approximate minima by plotting  $E_1$  level curves as a function of  $R_1$  in a small region around the minima. You can also plot the energy gradient and check the values of  $R_1$  that have gradient equal zero.

Table 1. Parameters for the Spin-Boson model. If you want to try a multidimensional model, too, values for  $j \neq 1$  are also suggested.

Parameter	Value (atomic units)
$\varepsilon_0$	0.03674933
$\nu_0$	0.03674933
$M_1$	1836
$\omega_1$	0.01136364
$g_1$	0.22
$M_j (j \neq 1)$	22032
$\omega_j (j \neq 1)$	0.00454545
$g_j (j \neq 1)$	0.10

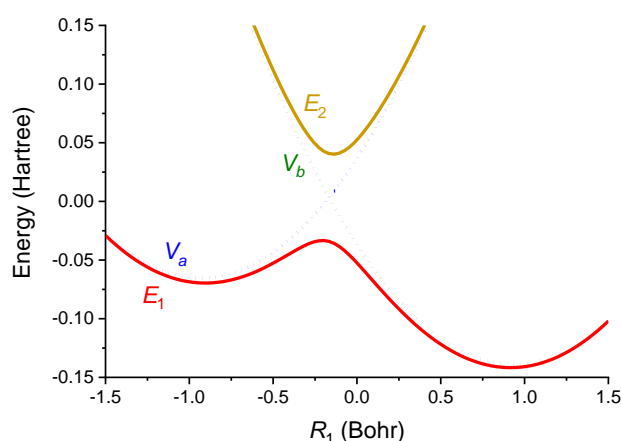


Figure 1. 1D cut along  $R_1$  direction of the Spin-Boson model given in Table 1.

### 3 Molecular dynamics (TP4)

One of the most popular algorithms to integrate Newton's second law is the Velocity Verlet<sup>2</sup>

$$\begin{aligned}\mathbf{R}_\alpha(t + \Delta t) &= \mathbf{R}_\alpha(t) + \mathbf{v}_\alpha(t)\Delta t + \frac{1}{2}\mathbf{a}_\alpha(t)\Delta t^2 \\ \mathbf{v}_\alpha(t + \Delta t) &= \mathbf{v}_\alpha(t) + \frac{1}{2}(\mathbf{a}_\alpha(t) + \mathbf{a}_\alpha(t + \Delta t))\Delta t\end{aligned}\quad (4)$$

where

$$\mathbf{a}_\alpha(t) = \frac{1}{M_\alpha} \left( -\frac{\partial E(\mathbf{R}(t))}{\partial \mathbf{R}_\alpha} + \mathbf{F}^{(e)} \right) \quad (5)$$

When these equations are applied to molecular dynamics,  $\alpha$  represents each nuclei of mass  $M_\alpha$  at Cartesian position  $\mathbf{R}_\alpha = (x_\alpha, y_\alpha, z_\alpha)$ , Cartesian velocity  $\mathbf{v}_\alpha = (v_{x,\alpha}, v_{y,\alpha}, v_{z,\alpha})$ , and Cartesian acceleration  $\mathbf{a}_\alpha = (a_{x,\alpha}, a_{y,\alpha}, a_{z,\alpha})$ .  $\Delta t$  is the integration step. In Eq. (5), the first term in the parenthesis is the potential energy gradient, and  $\mathbf{F}^{(e)}$  are external forces. The algorithm, including a total energy conservation check, is illustrated in Figure 2.

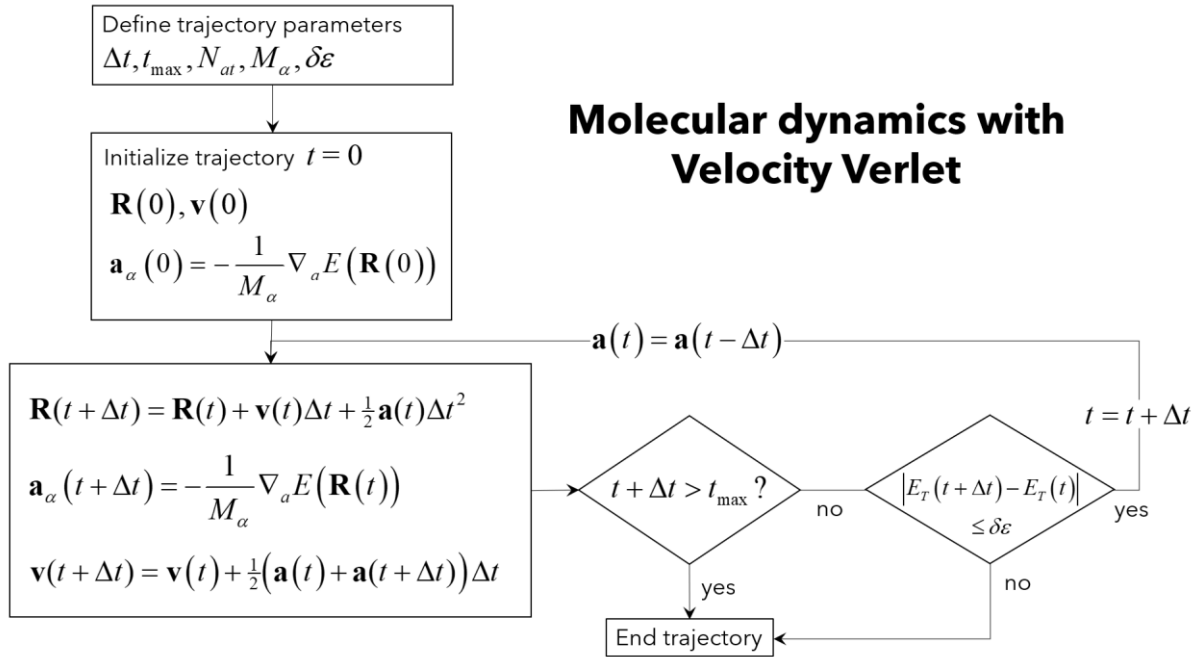


Figure 2. Schematic illustration of the Velocity Verlet algorithm.

**Task 4.** Implement an 1D Velocity Verlet algorithm for a single coordinate and without external forces. In this case, Eqs (4) and (5) simplify to

$$\begin{aligned}x(t + \Delta t) &= x(t) + v(t)\Delta t + \frac{1}{2}a(t)\Delta t^2 \\ v(t + \Delta t) &= v(t) + \frac{1}{2}(a(t) + a(t + \Delta t))\Delta t\end{aligned}\quad (6)$$

and

$$a(t) = -\frac{1}{M} \frac{dE(x(t))}{dx} \quad (7)$$

where  $x$  is the position,  $v$  is the velocity,  $a$  is the acceleration, and  $M$  is the mass.

**Tip.** Make a copy of the Notebook you created in TP3 and work on it.

**Tip.** Keep working in atomic units.

The total energy at time  $t$  is

$$E_T(t) = E_K(t) + E(t) \quad (8)$$

where the kinetic energy is

$$E_K(t) = \frac{1}{2} M v(t)^2 \quad (9)$$

The total energy is conserved if

$$|E_T(t) - E_T(t - \Delta t)| \leq \delta\varepsilon \quad (10)$$

where  $\delta\varepsilon$  is a parameter of the dynamics. Use  $\delta\varepsilon = 0.004$  au.

**Tip.** Your code will be better if you create separate functions to compute  $x$ ,  $v$ ,  $a$ ,  $E_K$ , and  $E_T$ .

**Task 5.** Run 1-ps (How much is that in atomic units of time?) dynamics on the  $E_1$  adiabatic PES given by the 1D model of Table 1. Start at a minimum of the left well (you found it in Task 3). Use total energy of approximately 0.1 Hartree. (If the system is at the minimum, the total energy equals the kinetic energy. Then, what's the initial velocity?) Does the total energy conserve during your trajectory? If not, either your program has a bug or  $\Delta t$  is too large. (A reasonable value is  $\Delta t = 20$  au.)

**Tip.** To compute the force (negative derivative of the potential energy) and the potential energy (needed to check the total energy conservation), use the functions that you implemented in TP3.

**Task 6.** Run the 1D model with different values of total energy, starting with all kinetic energy in  $R_2$ . What minimum energy is needed for the system to jump to the right well?

**Tip.** You can easily see the jump if you plot  $R_1$  as a function of time.

## 4 Thermostat (TP5)

In the previous TP, you ran microcanonical dynamics (constant energy). Now, let us run canonical dynamics (constant temperature). To do so, you should implement the Andersen thermostat.<sup>3</sup> The algorithm is the following:

- Define a collision frequency  $\Gamma$  (suggestion:  $\Gamma = 0.002$  au)
- Integrate dynamics in one step  $\Delta t$  with Velocity Verlet
- For each atom, sample a random number  $r_0$

If  $r_0 > \Gamma \Delta t$ , do not change the velocity

If  $r_0 \leq \Gamma \Delta t$ , change the velocity as

$$v^{(new)} = r_x \sqrt{\frac{k_B T}{M_\alpha}} \quad (11)$$

where  $r_x$  is another random number and  $k_B$  is the Boltzmann constant.

Both  $r_0$  and  $r_x$  are random numbers sampled from a Gaussian distribution of unit variance. They are not uniform random numbers!

**Task 7.** Implement the Andersen thermostat.

**Task 8.** Run dynamics of the 1D Spin Boson model at 300 K on the  $E_1$  adiabatic PES given in Table 1. Start at the left minimum with zero kinetic energy. How long does the trajectory take to reach 300 K? Have you seen jumps to the right well?

**Tip.** The temperature can be estimated as<sup>4</sup>

$$T \approx \frac{2 \langle E_{kin} \rangle}{N k_B}$$

where  $\langle E_{kin} \rangle$  is the mean kinetic energy and  $N$  is the number of dimensions. Thus, if you compute the moving average kinetic energy over the last, say, 200 integration steps, you can get  $T$  as a function of time.

**Task 9.** Estimate which temperature corresponds to the minimum total energy to have jumps you got in Task 6. (It should be in tens of thousands of Kelvin!) Run dynamics at this temperature. Do you see jumps?

## References

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