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Simple posterior frequency correction for vibrational spectra from molecular dynamics

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Vibrational spectra computed from molecular dynamics simulations with large integration time steps suffer from nonphysical frequency shifts of signals [M. Praprotnik and D. Janežič, J. Chem. Phys. 122, 174103 (2005)]. A simple posterior correction technique was developed for compensation of this behavior. It performs through replacement of abscissa in the calculated spectra using following formula: $V_{\text{corrected}} = \sqrt{\frac{2}{\Delta t}} e^{\frac{i(\cos(2\pi \Delta t v_{\text{initial}}) - 1)}{\Delta t}}$, where $v$ are initial and corrected frequencies and $\Delta t$ is the MD simulation time step. Applicability of this method was tested on gaseous infrared spectra of hydrogen fluoride and formic acid. Published by AIP Publishing. [http://dx.doi.org/10.1063/1.4948320]

I. INTRODUCTION

Molecular dynamic (MD) simulations are widely used for calculation of different molecular properties. Particularly, they can give vibrational spectra. In case of infrared absorption spectra, the results of MD simulation are converted into the frequency ($\nu$) vs. intensity ($I$) curve by the following equation:

$$I(\nu) \propto \frac{\nu \tanh \left(\frac{h\nu}{2kT}\right)}{n(\nu)} \text{Re} \int_0^\infty e^{-i2\nu t} (d(t), d(0)) dt,$$

(1)

where $d$ is dipole moment of the system, $(d(t), d(0)) = f(t)$ is autocorrelation function of the dipole moment, and $n(\nu)$ is refractive index. In case of gaseous spectra $n \approx 1$. It was found earlier that large time steps in the MD simulations lead to an overestimation of vibrational frequencies. Thus a recommendation was given to use small integration time steps in order to sample high frequency vibrations correctly. This sufficiently increases computational cost of MD simulations for calculation of vibrational spectra. Several solutions for this problems were suggested. They focus on modification of integration methods for equations of motion. For example, larger time steps can be used if high frequency bond stretch vibrations are treated analytically. However, these methods imply that some changes should be made in the software carrying MD simulations.

In the present work, we have tried to develop a simple technique for posterior correction of the spectra obtained from MD trajectories with different time steps. This correction was designed for classical Verlet (Störmer–Verlet) method. But other numerical integration techniques, such as velocity Verlet and leap-frog, are used more frequently for MD simulations. It is due to their better evaluation of atoms’ velocities: they are calculated directly during the simulation and their values are characterized by smaller errors. It can be shown that after elimination of velocities, these methods are algebraically equivalent to the Verlet integration. This fact was assumed to be rationale for transferability of the designed correction. Numerical tests of the obtained correction were done for the gaseous infrared spectra of hydrogen fluoride and formic acid.

II. DERIVATION OF THE CORRECTION

Let us consider a simple system: a one dimensional harmonic oscillator with the mass $\mu$ and potential $V(x) = \mu \omega^2 x^2/2$, where $\omega$ is angular frequency and $x$ is coordinate. Note, that experimental and calculated data are usually given in terms of frequencies $\nu = \omega/2\pi$. The solution for this system in the classical mechanics is $x = A \cos(\omega t + \phi_0)$, where $A$ is the amplitude of the vibration, $\phi_0$ is phase. Both parameters $A$ and $\phi_0$ are determined by initial conditions. Verlet integration is given by the following formula:

$$x_{n+1} = 2x_n - x_{n-1} + a_n \Delta t^2,$$

(2)

where $x_n$ denotes position, $a_{\Delta t}$ is acceleration on the $n$th step, and $\Delta t$ is the time increment. Obviously, in our case $a = -V_x/\mu = -\omega^2 x$. Therefore Eq. (2) takes form

$$x_{n+1} = x_n (2 - \omega^2 \Delta t^2) - x_{n-1}.$$

(3)

Let us assume that the result of integration can be expressed as $x_n = A \cos(\omega_0 \Delta t n + \phi_0)$, where $\omega_0$ is the effective frequency observed in the simulation. Obviously, $x_{n+1} = A (\cos(\omega_0 \Delta t n + \phi_0) \cos(\omega_0 \Delta t) \mp \sin(\omega_0 \Delta t n + \phi_0) \sin(\omega_0 \Delta t))$. Substitution of the $x_n$ and $x_{n+1}$ into Eq. (3) leads to the following expression:

$$\cos(\omega \Delta t) = 1 - \omega^2 \Delta t^2/2. \omega$$

stands here for the true frequency of the system, while $\omega_0$ represents effective frequency that is observed from numerical integration. Note that this equation is valid only if the $\omega \Delta t \ll 2$, since absolute value of cosine function cannot exceed 1. Therefore the

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correction will be given by the following formula:

$$\omega = \frac{\sqrt{2(1 - \cos(\omega \Delta t))}}{\Delta t}. \quad (4)$$

This equation defines a nonlinear transformation of the abscissa for the frequency vs. intensity spectra.

Let us use an inverse form of Eq. (4):

$$\omega = \frac{1}{\Delta t} \arccos(1 - \omega^2 \Delta t^2/2) \approx \omega(1 + \omega^2 \Delta t^2/24 + o(\omega^3 \Delta t^2))$$

in order to check properties of this replacement of coordinate system. We can see that \(\omega \to \omega_{\text{corr}}\). In other words, the smaller is time step or frequency, the closer is the observed value to the real one. And since \(\omega > 0 \Rightarrow \omega \geq \omega_{\text{corr}}\), the observed frequency is always shifted towards higher values with respect to the real one. These facts are in a good correlation with the known results.\(^9\)

### III. APPLICABILITY CHECK

#### A. Computational details

The chosen objects were hydrogen fluoride (HF) and formic acid (HCOOH). A cheap quantum chemical approximation PBE0/def2-SVP was used for numerical tests. Geometry optimizations for both molecules as well as calculation of Hessian and one dimensional potential energy scan for HF molecule were performed using Firefly program.\(^19\) \textit{Ab initio} MD simulations, VPT2-QFF (vibrational 2-nid order perturbation theory based on the expansion of potential energy surface up to quartic force field) calculations,\(^20\) and computation of Hessian in the case of HCOOH were done using GAMESS US software.\(^21\) PBE0 functional,\(^22\) VPT2-QFF anharmonic model,\(^20\) and Nose-Hoover thermostat\(^23,24\) were used as implemented in these programs. def2-SVP basis set\(^25\) was taken from Environmental Molecular Science Laboratory (EMSL) Basis Set Exchange Library.\(^26,27\) Integration of MD trajectories was performed using velocity Verlet method.\(^14\) A numerical solution of the time-independent one-dimensional Schrödinger equation for HF molecule was obtained using finite difference method as implemented in our in-house software. Conversion of the results of MD simulations into absorption spectra was performed using in-house AWK scripts. Smoothing of results of Fourier transformation given by Eq. (1) was performed with help of Gaussian window function \(w(t) = \exp(-t^2/\tau^2)\). \(\tau\) was 50 fs and 1 ps in cases of HF and HCOOH, respectively. Results of harmonic and VPT2-QFF approximations for HCOOH were converted into the intensity curve using Lorentzian profile function with half-width of 10 cm\(^{-1}\). This procedure was performed using Gbedit software.\(^28\)

#### B. Hydrogen fluoride: One dimensional vibration

Hydrogen fluoride (HF) molecule was chosen as a simple example. Only the bond stretch vibration was considered for this molecule and thus classical and quantum equations of motion that were used were one dimensional.

MD simulations with constant energy were performed. Three series of trajectories were obtained. They differed by initial conditions. Starting velocities of atoms were always set to zero, but the initial distance between the atoms was varied: 0.91, 0.89, and 0.87 Å. Therefore these series had different total energies. Time steps in each batch were 0.1, 0.5, 1.0, and 2.0 fs. It is important to note that 1.0 and 2.0 fs are inappropriate time steps. They violate the basic rule that requires time increment to be at least 10 times smaller than the period of the vibration (for the period of harmonic vibration for this system is 8 fs).\(^18,29\) Total length of every simulation was 1 ps. Absence of equilibration phase in this simple case was assumed. Translational and rotational degrees of freedom were eliminated by initial conditions.

Positions of the peaks’ maxims of the obtained spectra before and after the application of the correction defined by Eq. (4) can be found in Table I. There also are starting conditions and average temperature of simulation \(T_{\text{av}} = \sum m_i \langle v_i^2 \rangle/k_B N_f\), where \(m_i\) and \(\langle v_i^2 \rangle\) are the mass and average velocity of \(i\)th nucleus and \(N_f\) is the number of degrees of freedom (in our case \(N_f = 1\)).\(^16,18\)

It can be seen that in each series of simulations, the uncorrected frequency \(\bar{\nu}\) increases with the time step. This is in a good agreement with previous results\(^9\) and theoretical model. The corrected frequencies \(\nu_{\text{corr}}\) are always closer to each other than the uncorrected ones. In other words, the discrepancies in the \(\nu_{\text{corr}}\) are insignificant compared to the error arising from large time increment. It is interesting to note that \(T_{\text{av}}\) drops down with increase of \(\Delta t\) in each batch. This effect is caused by failure of energy conservation.

The more energy the system has, the more correct frequencies (\(\bar{\nu}\) for \(\Delta t = 0.1\) fs or \(\nu_{\text{corr}}\) for \(\nu \Delta t\)) are shifted towards lower values. It is the result of anharmonicity: the larger is the amplitude of vibration, the larger is the anharmonic frequency shift.\(^10,17\)

External standard values for the comparison were harmonic vibrational frequency \((\nu_{\text{harmonic}} = 3927\) cm\(^{-1}\) and energy difference between the zeroth and first vibrational levels \((\nu_{0 \to 1} = 3772\) cm\(^{-1}\)). \(\nu_{0 \to 1}\) was obtained from numerical solution of Schrödinger equation on the computed potential energy curve. Thus this value represents real anharmonic

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a Energy difference between equilibrium and starting geometries of simulation.

b Distance between H and F atoms at the beginning of simulation.

c Average temperature of the simulation (see text for explanation).
frequency. It can be seen that the uncorrected frequencies with the large time steps 0.5, 1.0, and 2.0 can even be larger than the $\nu_{\text{harmonic}}$. But corrected values tend to be $< \nu_{\text{harmonic}}$. However, they are still quite far from the quantum anharmonic frequency $\nu_{0\rightarrow1}$. This is again the result of the smaller amplitude of vibration in the classical system comparing to its quantum analog.\(^{10}\)

An illustration of the MD spectra in the case of simulation with the largest total energy (initial $r_{\text{HF}} = 0.87$ Å) and their comparison with the harmonic $\nu_{\text{harmonic}}$ and quantum anharmonic $\nu_{0\rightarrow1}$ frequencies can be found in Figure 1. It can be seen from this picture that the discussed correction can deform shape of initial intensity peak with the increase of $\Delta t$ (particularly, it reduces its width). But in the case of MD simulations, this width mainly comes from finite trajectory length and from the used window function. Therefore we consider this effect to be unimportant for discussion.

C. Formic acid: An example of polyatomic molecule

Formic acid was chosen for demonstration of applicability of the discussed correction for polyatomic molecules. In this case, MD-NVT simulations were performed. A single medium-length NVT simulation was chosen to avoid averaging of several short NVE trajectories as it was previously recommended.\(^{9,10}\) The NVT ensemble was simulated using chain of two Nose-Hoover thermostats. The chosen $\Delta t$ were 0.1 and 1.0 fs. 1.0 fs is also a badly chosen time step. Total length of the simulations was 7 ps. First 2 ps was ignored to account for the equilibration phase. Temperature of simulations was 300 K. Unfortunately, in both simulations, the O–H and C–H stretching vibrations were significantly affected by the “flying ice cube” effect: energy from these motions was drained into other degrees of freedom by the thermostat. As a result, relative intensities of the corresponding peaks in spectra were significantly lower than it was expected. Therefore comparison of the spectra for these vibrations was performed independently.

The reference theoretical spectra were harmonic and anharmonic. The last was computed using the VPT2-QFF model.\(^{20}\) A comparison with the experimental data from the NIST Chemistry Webbook Database was done as well.\(^{31}\) The illustration of range of frequencies 2800–4000 cm$^{-1}$ (i.e., bond stretching vibrations with the hydrogens) can be found in Figure 2, and of the range 450–2100 cm$^{-1}$ in Figure 3.

It can be seen from these figures that the corrected MD spectra computed from the trajectory with the time step 1.0 fs are very similar to those from 0.1 fs step simulation. Minor discrepancies of the peaks shape for the C–H and O–H stretching vibrations are probably caused by thermostat. The lower the frequency, the more the MD peaks are shifted from harmonic to VPT2-QFF ones. This is the result of transition from quantum to classical behavior with the lowering of energy. It is interesting to note that peaks of harmonic and MD spectra are aligned at one side with respect to the experimental ones, while VPT2-QFF frequencies can be found before and after them.

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**FIG. 1.** Vibrational spectra for HF molecule computed from MD simulations starting from 0.87 Å between H and F atoms with different time increments. Dashed and solid curves denote initial and corrected spectra, respectively. Solid vertical line represents anharmonic fundamental $0\rightarrow1$ transition frequency $\nu_{0\rightarrow1}$. Dashed vertical line stands for harmonic frequency $\nu_{\text{harmonic}}$.  

**FIG. 2.** Comparison of theoretical and experimental spectra of formic acid for C–H and O–H stretching vibrations. Dashed and solid curves for “MD” data denote initial and corrected spectra, respectively.  

**FIG. 3.** Comparison of theoretical and experimental spectra of formic acid excluding C–H and O–H stretching vibrations. Dashed and solid curves for “MD” data denote initial and corrected spectra, respectively.
IV. CONCLUSIONS

A simple posterior correction for MD vibrational spectra was developed. It accounts for frequency shift that comes from usage of large integration time steps. The calculated spectra should be replotted with new frequencies that are given by Eq. (4). Theoretical behavior of this correction function was found to be similar to previous numerical observations. This correction was constructed for the Verlet integration method. Applicability of this correction to other integration methods, such as velocity Verlet, was postulated on the basis of their algebraic equivalence. This assumption was then confirmed by performed numerical simulations that used velocity Verlet integration. Test objects were hydrogen fluoride (HF) and formic acid (HCOOH). The performed ab initio MD computations have shown that the correction restores frequencies of signal even in the cases of incorrectly chosen time steps. It was also found that this correction deforms shape of signals by reducing width of peaks with increase of the time increment. But this effect was considered insignificant since in case of spectra from MD this width mainly comes the finite length of trajectory.

Note that the developed correction regards only the integration technique and thus can be used for both force-field based and ab initio MD simulations.

Summing up, we can say that significant computational time savings for MD simulations can be achieved with use of the developed technique.

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