ISOTHERMAL QUANTUM DYNAMICS: NOSÉ-HOOVER DYNAMICS FOR COHERENT STATES

D. MENTRUP, J. SCHNACK
Universität Osnabrück, Fachbereich Physik
Barbarastr. 7, 49069 Osnabrück, Germany
E-mail: dmentrup@uos.de, jschnack@uos.de

The method of Nosé and Hoover[1,2] to create canonically distributed positions and momenta in classical molecular dynamics simulations is frequently used. Hamilton's equations of motion are supplemented by time-dependent pseudofriction terms that convert the microcanonical isoenergetic time evolution into a canonical isothermal time evolution, thus permitting the calculation of canonical ensemble averages by time averaging.
We show that for one *quantum* particle in an external harmonic oscillator, the equations of motion in terms of coherent states can easily be modified in an analogous manner to mimic the coupling of the system to a thermal bath and create a quantum canonical ensemble.[3] The method is generalized to a system of two identical quantum particles. In the resulting equations of motion, one obtains an additional attractive term for bosons and a repulsive term for fermions in the dynamics of the pseudofriction coefficients, leading to a correctly sampled thermal weight.

1 Coherent states

Coherent states[4] $|\, z \,\rangle = |\, r, p \,\rangle$ are eigenstates of the annihilation operator $\underset{\sim}{a}$ of the harmonic oscillator,

$$\underset{\sim}{a} \;|\, z \,\rangle = z \;|\, z \,\rangle \quad , \qquad z = \sqrt{\frac{m\omega}{2\hbar}}\, r + \frac{i}{\sqrt{2m\hbar\omega}}\, p \; . \tag{1}$$

In the coordinate representation one finds that coherent states are shifted Gaussian wavepackets that may be parameterized by the mean position r and the mean momentum p:

$$\langle\, x \,|\, z \,\rangle = \langle\, x \,|\, r, p \,\rangle \propto \exp\left\{ -\frac{(\,x - r\,)^2}{2}\frac{m\omega}{\hbar} + \frac{i}{\hbar} p\, x \right\} \; .$$

Since the set of coherent states forms a basis of the one-particle Hilbert space, this set may be used in order to evaluate canonical ensemble averages. Moreover, in the case of a harmonic oscillator potential, the thermal average of an observable $\underset{\sim}{B}$ may be written as an integral over the whole parameter space,[5]

$$\langle\langle\, \underset{\sim}{B} \,\rangle\rangle = \frac{1}{Z(\beta)} \int \frac{\mathrm{d}r\, \mathrm{d}p}{(2\pi\hbar)}\, w_{qm}(\beta; r, p)\, \mathcal{B}(r, p) \; , \tag{2}$$

with

$$Z(\beta) = \int \frac{\mathrm{d}r\, \mathrm{d}p}{(2\pi\hbar)}\, w_{qm}(\beta; r, p) \quad , \tag{3}$$

$$\mathcal{B}(r, p) = \langle\, r, p \,|\, \underset{\sim}{B} \,|\, r, p \,\rangle \; , \tag{4}$$

$$w_{qm}(\beta; r, p) = e^{-|z|^2 \left(e^{\beta\hbar\omega} - 1\right)} = e^{-\left(\frac{p^2}{2m} + \frac{1}{2} m\omega^2 r^2\right)\left(e^{\beta\hbar\omega} - 1\right)/(\hbar\omega)} \; . \tag{5}$$

Eq. (2) has the form of a classical phase space average, with $w_{qm}(r,p)$ being the thermal weight function on the parameter space.

The exact quantum time evolution of coherent states in a harmonic oscillator is expressed by the following equations of motion of the parameters r and p,

$$\frac{d}{dt}r = \frac{p}{m} \quad , \qquad \frac{d}{dt}p = -m\omega^2 r \; . \tag{6}$$

2 Quantum Nosé-Hoover thermostat

2.1 One particle

The equations of motion (6) are modified in a manner analogous to the classical Nosé-Hoover thermostat, i. e. a time-dependent pseudofriction term is added to the equation of motion of p. The dynamics of the pseudofriction coefficient is determined by the requirement that the resulting dynamics (7) samples the distribution function $w_{qm}(r,p)$. This requirement is expressed in terms of a Liouville equation in the parameter space $\Gamma = \{r, p, p_\eta\}$. One obtains the equations of motion

$$\begin{aligned} \frac{d}{dt}r &= \frac{p}{m} \quad , \qquad \frac{d}{dt}p = -m\omega^2 r - p\frac{p_\eta}{Q} \\ \frac{d}{dt}p_\eta &= \frac{1}{\beta}\left(\frac{p^2}{m}\frac{e^{\beta\hbar\omega}-1}{\hbar\omega} - 1\right) \; . \end{aligned} \tag{7}$$

Figure (1) compares the position and momentum distributions sampled by time averages to the exact marginal distributions of w_{qm}. As in the classical case, the simple Nosé-Hoover method features problems of non-ergodicity, i. e. not all parts of the phase space are sampled with the correct weight. This can be resolved by employing a chain of thermostats[6] or by the application of the closely related so-called KBB-thermostat.[7] Both methods sample the distribution $w_{qm}(r,p)$ correctly, and the mean value of any observable can be determined correctly by time averaging.

2.2 Two particles

In the case of two particles with a wavefunction $\langle\, x_1, x_2 \,|\, \hat{Z}\,\rangle$, the equation

$$\langle\langle \underset{\sim}{B} \rangle\rangle = \frac{1}{Z(\beta)} \int \frac{d^2 z_1}{\pi}\frac{d^2 z_2}{\pi} \underbrace{e^{-|z_1|^2(e^{\beta\hbar\omega}-1)} e^{-|z_2|^2(e^{\beta\hbar\omega}-1)} \langle\, \hat{Z} \,|\, \hat{Z}\,\rangle}_{w^{(2)}_{qm}(z_1,z_2)} \frac{\langle\, \hat{Z} \,|\, \underset{\sim}{B} \,|\, \hat{Z}\,\rangle}{\langle\, \hat{Z} \,|\, \hat{Z}\,\rangle} \tag{8}$$

defines $w^{(2)}_{qm}(z_1,z_2)$ as being the *thermal weight of the expectation value* $\frac{\langle\, \hat{Z} \,|\, \underset{\sim}{B} \,|\, \hat{Z}\,\rangle}{\langle\, \hat{Z} \,|\, \hat{Z}\,\rangle}$. In the case of fermions, we easily find $\langle\, \hat{Z} \,|\, \hat{Z}\,\rangle = \frac{1}{2}(1 - e^{-|z_1 - z_2|^2})$. This expression vanishes if $z_1 = z_2$ according to the Pauli exclusion principle. In contrast, for bosons we find $\langle\, \hat{Z} \,|\, \hat{Z}\,\rangle = \frac{1}{2}(1 + e^{-|z_1 - z_2|^2})$. The Nosé-Hoover equations of motion for the parameters $z_1 \equiv (r_1, p_1)$ and $z_2 \equiv (r_2, p_2)$ read

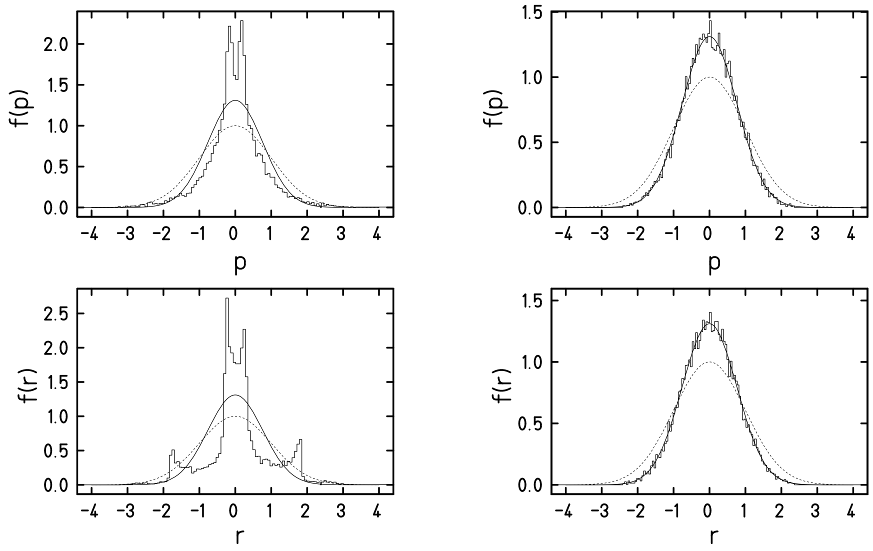

Figure 1. From above: momentum distribution, position distribution, left panel: Nosé-Hoover method according to the equations (7), right panel: Nosé-Hoover chain. The solid black line depicts the exact quantum result given by the respective partially integrated function w_{qm}/Z, e.g., $f(r) = \frac{1}{Z}\int \frac{dp}{\sqrt{2\pi\hbar}} w_{qm}(r,p)$, the dashed line represents the corresponding classical distribution $\propto e^{-\frac{p^2}{2m}+\frac{1}{2}\, m\omega^2 r^2}$ normalized to the same value. The distributions sampled by time averaging are presented as histograms.

$$
\begin{aligned}
\frac{d}{dt}r_1 &= \frac{p_1}{m} \quad , \qquad \frac{d}{dt}r_2 = \frac{p_2}{m} \\
\frac{d}{dt}p_1 &= -m\omega^2 r_1 - p_1\frac{p_{\eta_1}}{Q_1} \\
\frac{d}{dt}p_2 &= -m\omega^2 r_2 - p_2\frac{p_{\eta_2}}{Q_2} \ .
\end{aligned} \tag{9}
$$

The time dependence of the pseudofriction coefficients has to be determined in a procedure analogous to the case of a single particle. We obtain (upper sign for bosons, lower sign for fermions)

$$
\begin{aligned}
\dot{p}_{\eta_1} &= \frac{1}{\beta}\left(\frac{p_1^2}{m}\frac{e^{\beta\hbar\omega}-1}{\hbar\omega} - 1 \pm \frac{p_1(p_1-p_2)}{m\hbar\omega}\frac{1}{e^{|z_1-z_2|^2}\pm 1}\right) \\
\dot{p}_{\eta_2} &= \frac{1}{\beta}\left(\frac{p_2^2}{m}\frac{e^{\beta\hbar\omega}-1}{\hbar\omega} - 1 \mp \frac{p_2(p_1-p_2)}{m\hbar\omega}\frac{1}{e^{|z_1-z_2|^2}\pm 1}\right) \ .
\end{aligned} \tag{10}
$$

The part $\frac{p_i^2}{m}\frac{e^{\beta\hbar\omega}-1}{\hbar\omega} - 1$, $i = 1, 2$, in the equations of motion is familiar from the dynamics of a single thermostatted particle. However, in the case of two particles we find additional terms that reflect the effects of Bose-attraction and Pauli-blocking

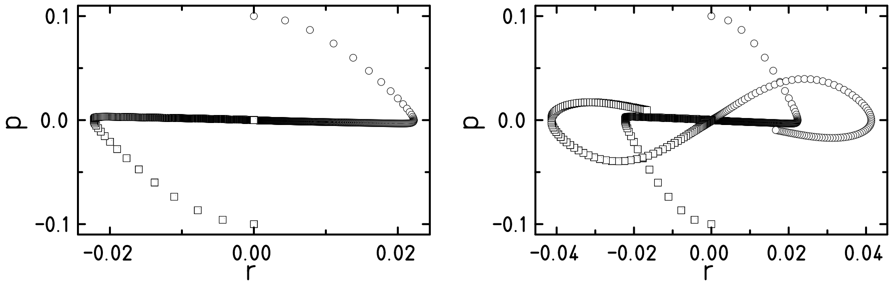

Figure 2. Left panel: isothermal dynamics of two identical bosons, right panel: two identical fermions. The equations of motion (9), (10) are integrated with the initial values $\{r_1, p_1, r_2, p_2\} = \{0, -0.1, 0, 0.1\}$ in both cases. The temperature is $T = 0.1\hbar\omega$, and $Q_1 = Q_2 = 0.5$. The integration time is 6.5 periods of the harmonic oscillator. The figure illustrates the effect of Bose attraction and Pauli-blocking on the dynamics: While the bosons stay close to each other for a certain time, the fermions are immediately driven away from each other due to the exclusion principle.

directly in the thermostatted dynamics, see figure (2). In essence, the effect of the thermostatted dynamics on identical quantum particles looks like an attractive or repulsive interaction, although we treat a system of non-interacting particles. The interaction is of purely statistical origin.

3 Outlook

We have presented a straightforward, yet non-trivial extension of the powerful techniques of heat bath coupling in classical molecular dynamics simulations to the quantum harmonic oscillator. Our goal is to extend the method to more general quantum systems, especially interacting fermion systems, using approximate quantum dynamics methods like Fermionic Molecular Dynamics.[8]

Acknowledgments

The authors would like to thank the Deutsche Forschungsgemeinschaft (DFG) for financial support of the project “Isothermal dynamics of small quantum systems”.

References

1. S. Nosé, *Prog. Theor. Phys. Suppl.* **103**, 1 (1991)
2. W. G. Hoover, *Phys. Rev.* A **31**, 1685 (1985)
3. D. Mentrup, J. Schnack, *Physica* A **297**, 337 (2001)
4. J. R. Klauder, B.-S. Skagerstam, Coherent states (World Scientific Publishing, Singapore, 1985)
5. J. Schnack, *Europhys. Lett.* **45**, 647 (1999)
6. G. J. Martyna et al., *J. Chem. Phys.* **97**, 2635 (1992)
7. D. Kusnezov, A. Bulgac, W. Bauer, *Ann. Phys. (NY)* **204**, 155 (1990)
8. H. Feldmeier, J. Schnack, *Rev. Mod. Phys.* **72**, 655 (2000)