Path Integral studies of quantum systems at finite temperatures

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Abstract

This thesis presents and develops the path integral simulation techniques in application to small quantum systems at finite temperatures. The first goal is to obtain exact thermodynamic expressions for systems of noninteracting identical particles in an arbitrary external field. The motivation comes from a desire to test simulation methods on systems with analytically calculated properties.

The rest and the major part of the thesis is dedicated to the development and testing of Bead-Fourier path integral molecular dynamics. Although, path integral molecular dynamics as well as path integral Monte Carlo are well known and developed, different computational and methodological problems still exist. These problems hinder application of path integrals to such a challenging problem as accurate, truly ab-initio calculation of electron structure in atoms and molecules. Thus, the development of a stable and reliable method is a necessity.

First, molecular dynamics under Bead-Fourier scheme was developed and tested on the examples of quantum harmonic oscillator and Hydrogen atom. The main attention was paid to ergodicity problems. Then we addressed the question, whether simulation scheme suggested, applied to electrons in the field of nuclei, is able to provide the accuracy level necessary for description of chemical bonds in molecules. It was found, that softening the Coulomb potential in the vicinity of the nucleus, lead to artificial behaviour of the electronic density. The correction potentials were introduced in an attempt to solve the problem. The method was developed for distinguishable particles and tested on one- and two-electron systems. The interaction potential between protons in Hydrogen molecule and molecular ion was reproduced. Later, the formalism for identical particles was developed.

Finally, the question of molecular dynamics efficacy was raised. It was shown, that formalisms for identical and distinguishable particles, both, can be reformulated into a more efficient ones, providing all dynamical variables to move on similar time scales.
to my family
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List of Papers

This thesis is based on the following publications and manuscripts

I. Quantum gas in an external field: Exact grand canonical expressions and numerical treatment.
P. N. Vorontsov-Velyaminov, S. D. Ivanov, R. I. Gorbunov.

II. Bead-Fourier path integral molecular dynamics.
S. D. Ivanov, A. P. Lyubartsev, and A. Laaksonen.

III. Simulations of one- and two-electron systems by Bead-Fourier path integral molecular dynamics.
S. D. Ivanov and A. P. Lyubartsev.

IV. Bead-Fourier path integral molecular dynamics for identical particles
S. D. Ivanov and A. P. Lyubartsev.
In manuscript.

The following related papers are not included in the thesis

V. Trapped mesoscopic quantum gas in a magnetic field.
P. N. Vorontsov-Velyaminov, R. I. Gorbunov and S. D. Ivanov.

VI. Bead-Fourier path integral Monte Carlo method applied to systems of identical particles.
P. N. Vorontsov-Velyaminov, R. I. Gorbunov and S. D. Ivanov.

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1 Introduction

Appearance and fast development of computers in the middle of the twentieth century inspired a breakthrough in many branches of science. Currently, the scientific investigations in physics, chemistry and biology can not be imagined without computers. In particular, besides solving equations numerically, computers allow to model systems of interest directly, creating a bridge between the theory and experiment. For instance, consider a molecular system, modeled on a computer. Besides the averaged properties, that can be compared with the experimental results, one has an access to any microscopic information at any instant. The latter possibility is very useful for understanding of the details and mechanisms of the processes, happening in the system. Many powerful and precise methods have been developed on the basis of the classical and statistical mechanics, allowing us to simulate complex molecular systems, e.g., liquids, biopolymers, electrolytes, plasmas, etc.

However, the classical description of molecular systems is not always satisfactory. Quantum mechanical description is required, when the de Broglie wavelength becomes comparable with the average distance between the particles in the system, i.e., the quantum delocalization effects become important. Usually it happens in either dense systems or at low temperatures. For electrons, due to their small mass, even room temperature is low, that is why they must be described quantum-mechanically at normal conditions. The other origin of a quantum mechanical behaviour is the quantum statistics, resulting in the (anti)symmetric properties of wavefunctions. Probably the best examples for systems of such a kind are liquid $^3$He and $^4$He. Superfluidity and superconductivity observed, are the collective exchange effects, which should be described by methods based on the quantum statistical mechanics.

Many such methods were developed. Part of them are based on the direct solution of the Schrödinger equation. Their disadvantage is that usually they allow us to obtain only the ground state, while we are often interested in the thermodynamics of the system at finite temperatures. The properties of the quantum systems at finite temperatures are described by the density matrix (partition function). The textbook expressions for the density matrix and partition function can not be used for computer simulations directly. So, they have to be transformed into a more suitable form. One way to do so is provided by Path Integral (PI) formalism [1, 2], resulting in the isomorphism between quantum particles and much more complicated, but classical objects. This, so-called, quantum-classical isomorphism [3] allows one to apply the power of well developed classical methods to the quantum statistical problems. In this thesis the molecular dynamics (MD) is chosen as such a classical method.

The idea of classical molecular dynamics is very simple: just to solve numerically the Newton’s equations of motion. In fact, it is done nowadays in
about the same way as astronomers in XVII-XIX centuries calculated the motion of planets. At that time, calculations were done mostly with pen and paper, and, possibly, mechanical calculators, which allowed to deal with the simultaneous motion of a few bodies. In spite of the imperfection of that times computational technique, it even managed to predict even an earlier unknown planet - Neptune, from the observed deviations in the calculated motion of Uranus.

Although, path integral molecular dynamics (PIMD) [4, 5] as well as path integral Monte Carlo (PIMC) [6] are well known and developed, different computational and methodological problems still exist. These problems hinder application of PI to such a challenging problem as accurate, truly ab-initio calculation of electron structure in atoms and molecules. Thus, the development of a stable and reliable method is a necessity, being one of the goals of this thesis.

Development of new computer simulation methods requires careful testing. One of the most convenient ways to test new techniques is to apply them for systems, with the exact solution known. Noninteracting quantum particles in the external field can be considered as an example of such systems. Although, analytical expressions for the canonical partition function, e.g., for two and three particles exist, they become more and more cumbersome with the growth of the particles’ number. However, the expressions for the grand canonical ensemble are often much more simple. Thus, the second goal of this thesis is to obtain exact expressions for systems of noninteracting identical particles in the external field.

Another reason of interest to the noninteracting particles is the noticeable amount of the experimental works on Bose-Einstein condensation (BEC) in trapped mesoscopic gases appeared during the last ten years (see, e.g. [7, 8, 9, 10]). Also, there exist works on a few confined electrons in the, so-called, quantum dots, e.g. [11, 12]. Those experiments increased the need in the analytical description of such kind of systems. Indeed, theoretical works appeared, investigating the thermodynamic properties of quantum gases confined by external fields (mainly harmonic or magnetic). Some of them are discussed in the Sec. 2.

The thesis is organised as follows. The historical overview of PI methods is presented in Sec. 2. The derivation of the PI formalism, the quantum-classical isomorphism as well as the quantum statistics and thermodynamics in terms of PIs are presented in Sec. 3. The details of the classical molecular dynamics methods and their application to PI are discussed in Sec. 4. The summary of the results and their discussion is presented in Sec. 5. The conclusions are summarized in Sec. 6.
2 Historical overview

Path integrals may be used in numerical computations and simulations, which allow one to obtain results even for complex many-body quantum systems. The idea of the PIs applied for quantum and statistical mechanics was suggested and developed by one of the most brilliant scientists of the twentieth century Richard Feynman [1, 2]. Feynman himself used PI mostly for illustration of the basic concepts of quantum mechanics and its relation to classical mechanics, as well as a tool for achieving approximate analytical results. According to Feynman the quantum partition function can be presented as an imaginary time PI, formally equivalent to the configurational integral over closed trajectories, or paths. It is also possible to extend it to a classical phase space integral. It turned out, that PI formulation of quantum and statistical mechanics is very suitable for numerical computations. Although the PI formalism is formally exact and straightforward to use for systems of interacting quantum particles, it requires, in principle, an infinite number of parameters to define the trajectory. Therefore, finite-number approximations have to be made in order to treat path integrals in numerical computer simulations, while the exact results are recovered in continuous limit only.

There exist many simulation techniques based on the Feynman PI formalism, which proved to be powerful and efficient for investigations of quantum many-body systems. PIs have found practical application in a very wide problems’ spectrum. Among them, liquids at low temperatures [13, 14, 15], fermion lattice models [16] and Wigner crystal [17], quantum effects on the motion of light nuclei [18, 19], plasmas [20, 21], atomic clusters [22, 23]. The list can be prolonged. Before passing to the simulation methods review, I would like to mention some analytical works dedicated to the noninteracting particles.

Brosens, Devreese and Lemmens published a series of works on those topics. In 1997, they published an article [24] describing the analytical formalism for the partition function of spinless identical harmonically coupled quantum particles in an external harmonic field. The main attention was paid to the thermodynamics of bosons. Density and pair correlation function was considered in [25]. The same ideas and results for fermions are presented in [26, 27]. However, the expressions obtained, are recurrent and quite cumbersome. Finally, they included the magnetic field into consideration and studied its influence on the thermodynamical properties and density of spin-polarized fermions [28, 29].

Already in 1967, Hohenberg [30] showed that the Bose-Einstein condensation (BEC) for particles in a box occurs only in three dimensions. However, Bagnato and Kleppner [31] demonstrated the possibility of BEC in an ideal Bose gas confined by one- and two-dimensional power-law traps. Kirsten and
Historical overview

Toms [32] considered the BEC of atomic gases in a three-dimensional general anisotropic harmonic confining potential in details. They discussed the differences of a confined system from an identical unconfined one. Ketterle and Druten [33] consider the impact of a finite number of particles on BEC, in particular, on the critical temperature shift. They also observed the presence of BEC in the lower-dimensional systems.

Fermionic systems were studied as well. In 1991 Johnson and Payne [34] investigated interacting fermions in a quantum dot. Their model consisted of two-dimensional harmonic well, homogenous magnetic field and harmonic coupling. They managed to obtain the spectrum of the energy states analytically. The noninteracting fermions in the harmonic traps were considered by Butts and Rokhsar [35] using the semiclassical (Thomas-Fermi) approximation.

Other ensembles, besides canonical, were used, namely, grand canonical and microcanonical. For instance, Balazs and Bergeman [36] considered thermodynamic variables obtained from microcanonical, canonical and grand canonical ensembles. For the first two, they derived the recursion relations that link partition functions for different dimensions. The fluctuations in general were discussed and expressions for variances of the atoms’ number, chemical potential and temperature for small fluctuations in the grand canonical ensemble were obtained. Lawson [37] presented path integral representation for the quantum microcanonical ensemble. He demonstrated the exact solutions for simple systems, such as the free particle and harmonic oscillator, while anharmonic oscillator was carried out by numerical integration.

For more realistic systems with non-harmonic interactions analytical approach is doomed to failure, and simulations become the only way to proceed. Here I would like to finish this brief description of works dedicated to the noninteracting particles and pass to the literature review of the simulation methods.

In this review, we shall consider, mainly, molecular dynamics [38] (MD) and Monte Carlo [39] (MC) methods. Historically, PI simulation techniques were applied initially within MC approach, so, we start from their review. One of the first practical studies was done by Fosdick and Jordan [40, 41, 42] who considered Wiener integrals mainly to compute Slater sums for $^4He$ at low temperatures. However, authors used both the PI representation and the MC technique and, thus, their works can be considered as the first practical implementation of PI within MC approach. Later, Morita [43] presented a solution of the Bloch equation for many-particle systems in terms of PI under different boundary conditions, in the form suitable for MC evaluation. Morita considered both Fermi and Bose statistics and it is worth mentioning that he was probably the first who faced the, so called, sign problem$^1$ and commented on it.

---

$^1$“Sign problem” occurs for fermions at low temperatures, when the ratio between positive
Another very interesting pioneer work was done by Miller [44] for quantum mechanical transition state theory. Among other achievements he developed the Feynman’s idea of PI representation by Fourier series, explicitly wrote down the corresponding Jacobian and made suggestions about the PI representation of the microcanonical density matrix. Barker [6] in 1979 introduced the discrete approximation to the Feynman PI, later referred as “bead” approximation and applied it to one and two hard particles in the one-dimensional hard-walled box, neglecting permutational symmetry. According to Barker, the trajectory was represented by beads connected via harmonic springs. This representation historically has become the most widespread. Those authors can be considered as pioneers of the PIMC simulations.

The PI techniques discussed above exploit the “quantum-classical isomorphism” [3, 45], i.e., the possibility to obtain the properties of quantum objects by classical simulations of ring trajectories. The quantum uncertainty is represented by substitution of a quantum particle by a trajectory, that is spread in space, with the size of the trajectory approximately equal to the de Broglie wavelength. The permutational symmetry leads to additional terms in the classical partition function. The formalism for the latter effect, referred as exchange, was developed within bead approximation for both Bose-Einstein and Fermi-Dirac statistics by Takahashi and Imada [46] in 1984. They also faced the sign problem (in the fermionic case) and invented the determinant approach (see Sec. 3.4) in order to alleviate it. Another way to bring in exchange effects into formalism was developed by Pollock and Ceperley [47] based on the density matrix (anti)symmetrization performed by summing over all permutations. Those two approaches would be discussed in details in Sec. 3.4.

In 1983 Doll and Freeman [48, 49] developed Fourier representation of PI for systems obeying quantum Boltzmann statistical mechanics, i.e., for distinguishable particles. In their approach the trajectory was approximated by a finite number of Fourier series terms, in contrary to discretized (bead) representation invented by Barker [6]. Enormous effort has been spent to determine which approach is superior and, in fact, this discussion continues up to nowadays (see, e.g. [50]) with no definite winner emerged. Coalson [51] suggested that “Perhaps this is because the two prescriptions are essentially the same”. Strictly speaking, both schemes come into perfect agreement only at very high orders of implementation. Later, Chakravarty introduced exchange within Fourier representation [52] and the basic formulations of both bead and Fourier schemes were completed.

I would like to comment on the work of Herman, Bruskin and Berne [53] which is of great methodological importance. Authors demonstrated that, so-called, primitive energy estimator used before, has the variance that grows as square root of beads number, and invented virial energy estimator, which is

and negative sign states tends to unity causing uncertainty growth. See Sec. 3.4 for details
used up to nowadays.

Anyhow, a few problems remained. First, the methods’ convergence was a problem of great importance. Strong attractive (e.g. Coulomb) fields require large numbers of beads to represent the trajectory under bead approximation, which in turn causes sampling and ergodicity problems as springs become too stiff. Under Fourier approximation it leads to slow convergence with the growth of Fourier amplitudes number. Second was the already mentioned sign problem, which appeared for fermionic systems at low temperatures. Both problems are the targets up to nowadays, although various recipes were suggested in attempts to solve or at least relax them.

Note, that in many cases, namely, for atomic liquids (except \(^4\)He) at any temperatures and for \(^4\)He up to \(5K\) it is possible to neglect exchange. Then, in those cases, only the convergence problem remained. Chandler and Wolynes [3, 45] introduced the interaction between trajectory beads, motivated by the variational theory. Coalson, Doll and Freeman [54, 55] developed “partial averaging” (under Fourier representation) in which first \(k_{\text{max}}\) Fourier harmonics were treated explicitly, while the high-order contribution (coming from \(k_{\text{max}} \ldots \infty \) harmonics) was included in an approximative way. Later, they generalized this idea to “cumulant” approach [56] which was not widely used due to increasing complexity. Several attempts were made to consider high order corrections to the Trotter expansion [57, 58, 59, 60]. Another idea arisen, was to expand the propagator in a power series [61, 62]. Perturbative corrections and their extrapolation [63] were also considered.

In 1997 the combined Bead-Fourier method was suggested by Vorontsov-Velyaminov et al. [64] “with an ordinary bead method and the Fourier PIMC method of Doll and Freeman being its extreme and non-optimal cases”.

Now, let us describe attempts to deal with the sign problem. As we already mention, the sign problem occurs for fermions at low temperatures and results in the exponentially growing uncertainty of the simulation results. Newman and Kuki [65] developed a technique mollifying the sign problem for two-fermion system by replacing a single position state with a set of rotationally equivalent states with partial cancellation of positive and negative contributions, reducing the uncertainty. The identification of statistically equivalent states for more than two fermions is, however, not trivial, hindering the extension to larger systems. Later, Hall generalized this idea by introducing projection operators [66]. In the other attempt to solve this problem, Ceperley suggested “restricted path integrals approach” [67] based on the generalized “fixed-node approximation”. It results in the simulation of only positively weighted terms, which obviously solves the sign problem. Ceperley stated that the approach is exact if the nodes are placed correctly and otherwise it is a fairly good approximation. Nevertheless, the correctness of this idea is doubtful as Filinov [68] showed that this scheme leads to incorrect result in the case
of a test system having an analytical solution (ideal Fermi gas). One of the most successful attempts to solve the sign problem was invented by Mak et al. entitled “multi-level blocking approach” [69, 70]. However, the price for the sign problem solution according to Mak et al. is the rapidly increased memory requirements.

Let’s turn attention to path integral molecular dynamics (PIMD) methods. The MD algorithm is used as an alternative to MC method to sample configurational space. Probably the first works on PIMD were done by Parrinello and Rahman [4] and Raedt, Sprik and Klein [5] in 1984. Authors considered an electron, described as quantum particle, solvated in molten KCl, which was presented classically [4]. Similarly, Muonium in water was simulated in [5]. Hall and Berne [71] pointed out that such dynamics is not ergodic, that is a MD algorithm does not sample the whole configurational space, leading to incorrect thermodynamical averages. The development of the canonical MD methods partially resolved that problem (see Sec. 4.3). Tuckerman et al. [72] developed staging MD in order to create an efficient PIMD.

Cao and Voth [73, 74, 75, 76] developed the formulation of quantum statistical mechanics based on the Feynman path centroid density. The latter played the role of the Boltzmann distribution in the classical statistical mechanics. The Centroid Molecular Dynamics (CMD) method was created, based on the formalism developed. Authors, themselves, considered CMD as a tool to target real-time quantum correlation functions. I would like to stress, that CMD itself is not a real quantum dynamics, but a quasi-classical approximation. CMD has been shown to be exact for a harmonic potential and proved to give a correct classical limit. Anyhow, those works caused deep resonance. Martyna [77, 78] tried to develop similar theory based on use of classical trajectories, generated by the true quantum mechanical potential of mean force. Jang and Voth [79] demonstrated that the time correlation functions obtained via CMD are related to the Kubo transformed quantum mechanical time correlation function for the case of linear operators. Reichman et al. [80] extended CMD for the case of nonlinear operators. Blinov and Roy developed an operator formulation of CMD both for Bose-Einstein and Fermi-Dirac statistics. Many other authors applied and extended this approach during last ten years. CMD was included as an option in the Car-Parrinello molecular dynamics package [81], now a standard tool in ab-initio MD simulations.

Filinov et al. [82] proposed real quantum dynamics based on Wigner representation.

Miura and Okazaki [83] developed a PIMD based on the determinant approach of Takahashi and Imada [46] and continued by inventing the PIMD based on the pair density matrix approximation [84]. We, ourselves, developed a Bead-Fourier PIMD [85, 86], following the ideas of Vorontsov-Velyaminov et al. [64], which is the main subject of this thesis.
3 Path Integrals in the canonical ensemble

3.1 From basics to Path Integrals

Consider a single quantum particle with mass \( m \) in a one-dimensional potential \( \phi(x) \) described by a Hamiltonian:

\[
\hat{H} = \frac{\hat{p}^2}{2m} + \phi(\hat{x}) \equiv \hat{K} + \hat{\Phi}
\]  

(1)

where \( \hat{K} \) and \( \hat{\Phi} \) are the kinetic and potential energy operators, respectively, \( \hat{p} \) and \( \hat{x} \) being the momentum and coordinate operators. In quantum statistical mechanics we do not consider quantum eigen states of given energy \( E \), but suppose instead, that particles interact with a heat bath, or "thermostat", of temperature \( T \). Specifically, we consider only canonical (NVT) ensemble, although path integrals can be formulated in a variety of statistical ensembles (e.g., isothermal-isobaric NPT ensemble [87]). The density matrix and partition function for the canonical ensemble are given by:

\[
\hat{\rho} = \exp\left[-\beta \hat{H}\right], \quad Z(\beta) = \text{Tr} (\hat{\rho})
\]  

(2)

where \( \beta \equiv 1/kT \) is the inverse temperature. Let us consider density matrix (2) in the coordinate representation (Note, that the partition function (2), being the trace of the density matrix, is independent on the representation in which it is evaluated):

\[
\rho(x; x') = \langle x | \exp\left[-\beta \hat{H}\right] | x' \rangle = \langle x | \exp\left[-\beta \left( \hat{K} + \hat{\Phi} \right) \right] | x' \rangle
\]  

(3)

In general, the kinetic and potential energy operators (\( \hat{K} \) and \( \hat{\Phi} \)) do not commute and Trotter theorem [88] can be applied in order to evaluate exponent in (3). Trotter theorem states, that for any two operators \( \hat{A} \) and \( \hat{B} \):

\[
\exp \left( \hat{A} + \hat{B} \right) = \lim_{n \to \infty} \left[ \exp \left( \frac{\hat{B}}{2n} \right) \exp \left( \frac{\hat{A}}{2n} \right) \exp \left( \frac{\hat{B}}{2n} \right) \right]^{n}
\]  

(4)

Expansion of expression for the density matrix (3), according to the Trotter theorem (4), yields:

\[
\rho(x; x') = \lim_{n \to \infty} \langle x | \hat{\Omega}_n^x | x' \rangle,
\]

\footnote{Here we use the symmetrized form of the Trotter expansion, although non-symmetrized form can be used here as well. In Sec. 4.2 we shall show that it is more convenient for developing time-reversible MD integrators.}
\[ \hat{\Omega}_n \equiv \exp \left[ -\frac{\beta \Phi}{2n} \right] \exp \left[ -\frac{\beta \hat{K}}{n} \right] \exp \left[ -\frac{\beta \Phi}{2n} \right] \] (5)

where operator \( \hat{\Omega}_n \) is introduced for briefness of notations. Since fraction \( \beta/n \) can be treated as new inverse temperature \( \beta' \), which is \( n \) times smaller (and temperature is \( n \) times higher, correspondingly), Eq. (5) has the sense of a high temperature expansion. Since the coordinate-space eigenvectors form a complete basis set, the identity operator can be introduced as:

\[ \hat{1} = \int dx \mid x \rangle \langle x \mid \] (6)

and inserted in between each pair of factors of \( \hat{\Omega}_n \) in (5). Since there are \( n \) operators in the product, \( n - 1 \) insertions should be done. Let us label the integration variables as \( x_2, x_3, \ldots, x_n \) and write down the equation for the density matrix:

\[ \rho (x; x') = \lim_{n \to \infty} \int dx_2 \cdot dx_3 \ldots dx_n \langle x \mid \hat{\Omega}_n \mid x_2 \rangle \langle x_2 \mid \hat{\Omega}_n \mid x_3 \rangle \ldots \langle x_n \mid \hat{\Omega}_n \mid x' \rangle \] (7)

Finally, the partition function \( Z(\beta) \) is:

\[ Z(\beta) = \lim_{n \to \infty} \int dx_1 \ldots dx_n \langle x_1 \mid \hat{\Omega}_n \mid x_2 \rangle \ldots \langle x_n \mid \hat{\Omega}_n \mid x_1 \rangle = \lim_{n \to \infty} \int \prod_{j=1}^{n} dx_j \langle x_j \mid \hat{\Omega}_n \mid x_{j+1} \rangle \] (8)

where \( x \) and \( x' \) are denoted as \( x_1 \) and \( x_{n+1} \), respectively, in order to unify the formula, under restriction \( x_1 = x_{n+1} \) being the result of a trace operation. Now, we investigate matrix elements of \( \hat{\Omega}_n \):

\[ \langle x_j \mid \hat{\Omega}_n \mid x_{j+1} \rangle = \langle x_j \mid \exp \left[ -\frac{\beta \Phi}{2n} \right] \exp \left[ -\frac{\beta \hat{K}}{n} \right] \exp \left[ -\frac{\beta \Phi}{2n} \right] \mid x_{j+1} \rangle \] (9)

Potential energy operator \( \Phi \) is a function of coordinates only, and, thus, can be applied for coordinate eigenfunctions directly, resulting in their eigenvalues:

\[ \langle x_j \mid \hat{\Omega}_n \mid x_{j+1} \rangle = \exp \left[ -\frac{\beta \phi (x_j)}{2n} \right] \langle x_j \mid \exp \left[ -\frac{\beta \hat{K}}{n} \right] \mid x_{j+1} \rangle \exp \left[ -\frac{\beta \phi (x_{j+1})}{2n} \right] \] (10)
Path Integrals in the canonical ensemble

The matrix elements of \(\exp(-\beta \hat{K}/n)\) can be evaluated in the similar manner, by introduction of another completeness relation for momentum eigenstates:

\[
\hat{I} = \int dp \langle p | p \rangle
\] (11)

and following insertion of \(\hat{I}\) (11) into Eq. (10). By using the well known quantum mechanical relation:

\[
\langle x | p \rangle = \frac{1}{\sqrt{2\pi\hbar}} \exp\left(\frac{ipx}{\hbar}\right)
\] (12)

we find that:

\[
\langle x_j | \exp\left[\frac{-\beta \hat{K}}{n}\right] | x_{j+1} \rangle = \frac{1}{2\pi\hbar} \int dp \exp\left[\frac{-\beta p^2}{2mn}\right] \cdot \exp\left[-\frac{i p(x_{j+1} - x_j)}{\hbar}\right]
\] (13)

Performing the integration by completing the square under the exponential, we arrive at the, so-called, discretized form of path integral for the density matrix elements, written in a general form:

\[
\rho(x; x') = \lim_{n \to \infty} \left(\frac{m n}{2\pi \beta \hbar^2}\right)^{n/2} \exp\left[-\frac{\beta}{2n} (\phi(x) + \phi(x'))\right] \cdot \int dx_2 \ldots dx_n \exp[-\beta U_{\text{eff}}(\{x_j\})]
\] (14)

where the effective potential \(U_{\text{eff}}\),\(^3\)

\[
U_{\text{eff}}(\{x_j\}) \equiv \frac{mn}{2\beta \hbar^2} \sum_{j=1}^{n} (x_{j+1} - x_j)^2 + \frac{\beta}{n} \sum_{j=2}^{n} \phi(x_j)
\] (15)

with \(x_1 \equiv x\) and \(x_{n+1} \equiv x'\). The corresponding discretized form of path integral for the partition function reads:

\[
Z(\beta) = \lim_{n \to \infty} Z_n(\beta) = \left(\frac{m n}{2\pi \beta \hbar^2}\right)^{n/2} \int dx_1 \ldots dx_n \exp[-\beta U_{\text{eff}}(\{x_j\})]
\] (16)

with cyclic condition: \(x_{n+1} = x_1\). In fact, the expression for the partition function \(Z_n(\beta)\) (16) already provides the way for practical simulations, as we shall show below.

\(^3\)The sense of the denotation will be explained later.
The continuous limit and imaginary time path integral

It is worth mentioning, that the factor prior the quadratic term in the exponential in Eq. (15), as well as the normalization factor, can be expressed in terms of de Broglie thermal wavelength, that corresponds either to the inverse temperature $\beta$, or to the inverse temperature $\beta/n$:

$$
\Lambda \equiv \sqrt{\frac{2\pi \beta \hbar^2}{m}}, \quad \Lambda_n \equiv \sqrt{\frac{2\pi \beta \hbar^2}{mn}}
$$

(17)

Obviously, the variable transform can be made: $\tilde{x}_j \equiv x_j/\Lambda$ (the same, naturally, can be done with $\Lambda_n$). Then the expression for $Z_n(\beta)$ will look like:

$$
Z_n(\beta) = n^{n/2} \int d\tilde{x}_1 \ldots d\tilde{x}_n \exp \left\{ -\sum_{j=1}^{n} \left[ \pi n (\tilde{x}_{j+1} - \tilde{x}_j)^2 + \frac{\beta}{n} \tilde{\phi}(\tilde{x}_j) \right] \right\}
$$

(18)

where $\tilde{\phi}(\tilde{x}_j) \equiv \phi(x_j)$. Thus, the partition function and, hence, all thermodynamic properties can be naturally expressed via coordinates, scaled by the de Broglie wavelength $\Lambda$ (17).

### 3.2 The continuous limit and imaginary time path integral

The next step is to demonstrate the continuous limit, i.e., $n \to \infty$. It is interesting to note, that expression for the matrix elements of the quantum time evolution operator $\exp \left[ -it\hat{H}/\hbar \right]$ can be obtained from Eq. (14) by formal setting: $\beta \equiv it/\hbar$. We shall excurse to the consideration of the evolution operator and return back to the density matrix afterwards. So, the path integral expression for the quantum time evolution operator is as follows:

$$
\langle x | \exp \left( -\frac{it}{\hbar} \hat{H} \right) | x' \rangle = \lim_{n \to \infty} \left( \frac{mn}{2\pi it\hbar} \right)^{n/2} \exp \left[ -\frac{it}{2n\hbar} (\phi(x) + \phi(x')) \right] \cdot
$$

$$
\int dx_2 \ldots dx_n \exp \left\{ \frac{imn}{2t\hbar} \sum_{j=1}^{n} (x_{j+1} - x_j)^2 - \frac{it}{n\hbar} \sum_{j=2}^{n} \phi(x_j) \right\}
$$

(19)

with the same denotations: $x_1 \equiv x$ and $x_{n+1} \equiv x'$. In order to illustrate the appearance of the imaginary time, we shall obtain the continuous form of the quantum evolution operator (19). First, let us introduce a parameter:

$$
e \equiv \frac{t}{n}
$$

(20)

and substitute it in Eq. (19). We assume, that the limit $n \to \infty$ exists and change the order of the integration and the limit operation. Note also, that the
limit $n \to \infty$ is equal to limit $\epsilon \to 0$, if we consider fixed time interval $t$. For briefness, we consider only the inner part of Eq. (19):

$$
\lim_{n \to \infty, \epsilon \to 0} \left[ \frac{i \epsilon}{\hbar} \sum_{j=1}^{n} \frac{m}{2} \left( \frac{x_{j+1} - x_{j}}{\epsilon} \right)^2 - \frac{i \epsilon}{2\hbar} (\phi(x) + \phi(x')) - \frac{i \epsilon}{\hbar} \sum_{j=2}^{n} \phi(x_j) \right]
$$

(21)

Since, $n \to \infty$ means that the number of points $x_j$ tends to infinity and $x_{j+1}$ must be close to $x_j$ due to exponential factor $\exp[-(x_{j+1} - x_j)^2]$, the points $x_j$ can be treated as specific points of continuous function $x(s), s \in [0; t]$, such that $s \equiv (j - 1)\epsilon, x(s) \equiv x_j = x((j - 1)\epsilon)$ with $x(0) = x, x(t) = x'$. Thus, all items appearing in (21) can be easily recognized, e.g.:

$$
\lim_{\epsilon \to 0} \frac{x_{j+1} - x_j}{\epsilon} = \lim_{\epsilon \to 0} \frac{x(j\epsilon) - x((j - 1)\epsilon)}{\epsilon} = \frac{dx}{ds}.
$$

(22)

Moreover, sums in the exponential under the limit are the Riemann sums, which can be transformed to a continuous integral:

$$
\frac{i}{\hbar} \int_{0}^{t} ds \left[ \frac{m}{2} \left( \frac{dx}{ds} \right)^2 - \phi(x(s)) \right].
$$

(23)

Finally, consider the integration measure:

$$
\left( \frac{m}{2\pi i \hbar} \right)^n dx_1 \ldots dx_n
$$

(24)

As we already mentioned, as $n \to \infty$ and $\epsilon \to 0$ the number of points becomes infinite and they become infinitely closely spaced. Thus, the integration over all infinite amount of points can be treated as integration over all continuous functions $x(s)$ or, in other words, functional integration. Finally:

$$
\langle x | \exp \left( -\frac{it}{\hbar} \hat{H} \right) | x' \rangle = \int_{x}^{x'} Dx(s) \exp \left\{ \frac{i}{\hbar} \int_{0}^{t} ds \left[ \frac{m}{2} \left( \frac{dx}{ds} \right)^2 - \phi(x(s)) \right] \right\}
$$

(25)

where the special notation $Dx(s)$ represents functional integration:

$$
Dx(s) \equiv \lim_{n \to \infty, \epsilon \to 0} \left( \frac{m}{2\pi i \hbar} \right)^n dx_1 \ldots dx_n
$$

(26)

Eq. (25) is known as functional integral representation of the path integral. Practically, it represents the integration over all continuous paths (functions $x(s)$ can be treated as paths between space points $x$ and $x'$) with boundary conditions $x(0) = x$ and $x(t) = x'$. 


The form of the integrand under exponential in Eq. (25) is well known in the classical mechanics being the Lagrangian:

\[ L(\dot{x}; x) = \frac{m}{2} \dot{x}^2 - \phi(x) \]  

(27)

The integral of a Lagrangian over specific path \( x(s) \) is known as action:

\[ S [x(s)] = \int_0^1 ds L(\dot{x}(s); x(s)) \]  

(28)

and plays an important role in classical mechanics. In classical mechanics one should take into account only the path chosen according to the least action principle. The quantum mechanical rule is different. Richard Feynman in his lectures [1] wrote: “It is not just the particular path of extreme action contributes; rather, it is that all the paths contribute. They contribute equal amounts to the total amplitude, but contribute at different phases. The phase of contribution is the action \( S \) for that path in units of the quantum of the action \( \hbar \).” Note, that the classical limit can be obtained straightforwardly [1]: with \( \hbar \to 0 \) all paths except those, for which \( \delta S = 0 \) will oscillate wildly, leading to positive and negative contributions that largely cancel out.

Turning back to the density matrix we note, that expression for the evolution operator was obtained from the one for the density matrix by substitution \( \beta = it/\hbar \). Thus, the inverse transformation can be obtained by setting \( t = -i\beta \hbar \) or, in other words, by letting time be imaginary. That is why the canonical density matrix is often referred to as imaginary time or Euclidean (because the expression itself becomes real) propagator. Finally, path integral expression for the density matrix is:

\[
\langle x | \exp \left( -\beta \hat{H} \right) | x' \rangle = \int_x^{x'} Dx(\tau) \exp \left\{ -\frac{1}{\hbar} \int_0^{\beta \hbar} d\tau \left[ \frac{m}{2} \left( \frac{dx}{d\tau} \right)^2 + \phi(x(\tau)) \right] \right\}
\]

(29)

where \( \tau \) is the imaginary time, \( \tau \in [0; \beta \hbar] \) and the integration is carried out along all paths \( x(\tau) \) starting at \( x \) and ending at \( x' \). Eq. (29) is known as a continuous imaginary time path integral. Analogously, the integrand under the exponential is called the Euclidean Lagrangian:

\[ \mathcal{L}(\dot{x}; x) = \frac{m}{2} \dot{x}^2 + \phi(x) \]

(30)

Note, that Euclidean Lagrangian \( \mathcal{L}(\dot{x}; x) \) is the sum of potential and kinetic energies in contrary to Lagrangian \( L(\dot{x}; x) \) (27) which is their difference. And

---

4Basics of the classical mechanics are briefly described in Sec. 4.1.
the integral over a continuous imaginary path $x(\tau)$ is called, respectively, the Euclidean or imaginary time action:

$$S[x(\tau)] = \int_0^{\beta\hbar} d\tau \mathcal{L}(\dot{x}(\tau); x(\tau))$$

The final expression for partition function $Z(\beta)$ then looks like:

$$Z(\beta) = \int dx \int_{x[0]}^{x(\beta\hbar)} Dx(\tau) \exp \left\{ -\frac{1}{\hbar} S[x(\tau)] \right\}$$

with $x(0) = x(\beta\hbar)$. The latter expression means that the integration should be carried out with respect to all closed imaginary time paths that begin and end at the same point $x$, and then the separate integration should be performed over all space points $x$.

I would like to stress, that up to this point the formalism developed is exact. Indeed, we have not done any approximations yet.

### 3.3 Quantum-classical isomorphism and different representations of the trajectory

In the previous subsections we described a path integral formalism, which turned out to be very elegant and exact. From the practical point of view, one needs a technique that would allow to simulate quantum objects directly, as the classical systems are simulated. So, the purpose is to find a classical analogue of the quantum particle and apply the power of well developed classical methods to its investigation. Path integral formalism provides us with such a way.

In fact, Eq. (32) states, that if one wants to examine canonical properties of a quantum particle, one can consider an ensemble of closed imaginary time paths. Anyhow, the form achieved is not suitable for practical simulations. Since a description of a trajectory (or a path) in the general form requires an infinite number of parameters, one has to make a finite-number approximation. As it was already mentioned, Eq. (16) provides us with one of the possible approximations known as bead approximation [6]. Let us illustrate the idea by rewriting Eqs. (16) and (15):

$$Z_n(\beta) = \left( \frac{mn}{2\pi \beta\hbar^2} \right)^{n/2} \int dx_1 \ldots dx_n \exp \left[ -\beta U_{\text{eff}}(x_1, \ldots, x_n) \right]$$

where the effective potential $U_{\text{eff}}(x_1, \ldots, x_n)$ is:
Quantum-classical isomorphism

\[ U_{\text{eff}}(x_1, \ldots, x_n) \equiv \sum_{j=1}^{n} \left[ \frac{m \omega_n^2}{2} (x_{j+1} - x_j)^2 + \frac{1}{n} \phi(x_j) \right]_{x_{n+1}=x_1} \]  

(34)

the “chain frequency” \( \omega_n \) being:

\[ \omega_n \equiv \frac{\sqrt{n}}{\beta \hbar} \]  

(35)

The Eq. (33) is recognized as the classical configurational partition function for a \( n \)-particle system, which looks like a beaded necklace. Therefore, those \( n \) particles are usually referred as beads. Those beads are connected by harmonic springs with equilibrium distance equal to zero and frequency \( \omega_n \) defined in (35).

Finally, we can conclude that we proceeded from the expression for the quantum canonical partition function of a single particle to the classical partition function which corresponds to the \( n \)-particle system. This is called quantum-classical isomorphism [3]. In other words, one can simulate the classical system described by the Hamiltonian (34) and the partition function (33) by means of, e.g., classical Monte Carlo method and obtain the canonical properties of the quantum particle. It should be underlined, that “true” properties of the quantum systems are recovered only in the limit \( n \to \infty \).

Bead representation is not the only known form for discretized path integral. Doll and Freeman [48, 49] suggested another finite-number approximation. Let us start from Eq. (32) for the partition function. The idea is to expand the path in a Fourier series about a fixed path that connects \( x \) and \( x' \):

\[ x(\xi) = x + (x' - x) \xi + \sum_{k=1}^{\infty} a_k \sin(k\pi \xi) \]  

(36)

with substitution \( \xi \equiv \tau / \beta \hbar \) performed. The “fixed path” here is chosen to be linear. If we substitute the chosen trajectory representation (36) into the expression for partition function (32), the integration of the kinetic term over \( \xi \) can be evaluated analytically, using the fact that cosines form the complete orthogonal system of functions. Remembering, that under trace \( x \) becomes equal to \( x' \), i.e., we consider closed paths, and transforming functional integration into integration over Fourier amplitudes, one obtains:

\[ Z(\beta) = J \prod_{k=1}^{\infty} \int d\alpha_k \exp \left[ - \frac{m}{2\beta \hbar^2} \frac{(\pi k)^2}{2} - \frac{\alpha_k^2}{2} \right] \cdot \exp \left\{ -\beta \int_0^1 d\xi \phi(x(\xi)) \right\} \]  

(37)

Here \( J \) is the Jacobian of the transformation from the integral over all paths to integral over all Fourier amplitudes [44, 49]. For our purposes, it is enough
to know that this Jacobian is a constant, in the sense, that it is independent both from coordinates and the form of the potential. Expression (37) is still exact, as long as trajectory is represented with the infinite number of Fourier sine series terms. In order to adopt it for practical simulations, we truncate the series at some term with the number denoted as $k_{\text{max}}$. However, we do not know any universal recipe to determine the proper value of $k_{\text{max}}$ beforehand, i.e., without test simulations.

It was shown [51] that Bead and Fourier approximations are essentially the same in the high-order implementation, in other words, when the number of parameters representing the trajectory is large enough. Thus, the choice of the parametrization should be done according to efficiency, which can vary substantially depending on the particular system and the specific algorithm.

The combined Bead-Fourier (BF) method was introduced by Vorontsov-Velyaminov et al. [64]. The basic idea behind the BF approach is to unite the Bead and Fourier approximations within a single scheme. Namely, the trajectory $x(\tau)$, describing the quantum particle, is presented as a set of beads, connected by continuous paths expressed as Fourier sine series. Let us again start from Eq. (32) for the partition function. We split the imaginary time interval $[0; \beta \hbar]$ into $n$ equal (though it is not necessary) pieces and introduce the following notations: $\tau_1 = 0$, $\tau_2 = \beta \hbar / n$, $\tau_j = (j - 1) \beta \hbar / n$, $\tau_{n+1} = \beta \hbar$. Let also $x(\tau_j)$ be equal to $x_j$ with respect to cyclic property $x(\tau_{n+1}) = x_1 = x$. Then the partition function becomes:

$$Z(\beta) = \prod_{j=1}^{n} \int dx_j \int_{x_j}^{x_{j+1}} Dx(x(\tau) \exp \left\{ -\frac{1}{\hbar} S_j [x(\tau)] \right\} \right.$$  

(38)

where $S_j [x(\tau)]$ is the Euclidean action, corresponding to the imaginary time slice $[\tau_j; \tau_{j+1}]$:

$$S_j [x(\tau)] \equiv \int_{\tau_j}^{\tau_{j+1}} d\tau \left[ \frac{mz^2(\tau)}{2} + \phi(x(\tau)) \right]$$  

(39)

Now, we perform the same expansion of the trajectory, as we have done during the pure Fourier approximation development (36), but for each Euclidean time slice separately:

$$x_j(\xi) = x_{j+1} - x_j + \sum_{k=1}^{k_{\text{max}}} a_{j,k} \sin (k\tau \xi)$$  

(40)

where $\xi \equiv n(\tau - \tau_j)/\beta \hbar$. Note, that here the Fourier sine series was truncated from the very beginning. In fact, further development is completely similar to the pure Fourier case. The final expression for the partition function looks like:
Quantum statistics. Identical particles

\[ Z(\beta) = C(\beta) \int \exp \left\{ -\beta H \left( \{x_j, a_{jk}\} \right) \right\} \prod_{j=1}^{n} \left( dx_j \prod_{k=1}^{k_{\max}} da_{jk} \right) \]  

(41)

where the effective Hamiltonian \( H \) is:

\[ H(\{x_j, a_{jk}\}) = \sum_{j=1}^{n} \left\{ \frac{mn}{2\beta^2 \hbar^2} \left( x_{j+1} - x_j \right)^2 + \sum_{k=1}^{k_{\max}} \frac{3(3k^2 + 1)}{24} a_{jk}^2 \right\} + \frac{1}{n} \int_{0}^{1} d\xi \phi(x_j(\xi)) \]  

(42)

\( C(\beta) \) being the normalization constant. Thus, we have \( n(1 + k_{\max}) \) generalized coordinates: \( n \) beads’ coordinates \( x_j \) and \( n \cdot k_{\max} \) Fourier amplitudes \( a_{jk} \).

It is clear, that Bead-Fourier approach contains both Bead and Fourier approximations as limiting cases. Indeed, if we set \( n = 1 \) in Eq. (41) then we get the expression (37). If we set \( k_{\max} = 0 \) and use the trapezoid rule approximation for the integral of the potential \( \phi \) then the result would coincide with the partition function, corresponding to the pure bead case (33).

Note, that although the formalism for all methods presented above was developed for a single quantum particle in one dimension, the generalization for the case of many particle \( d \)-dimensional system is straightforward, see, for instance Ref. [64]. Also note, that the described formalism corresponds to the case of distinguishable particles, i.e., Boltzmann statistics. The generalization for the case of identical particles with permutational symmetry is presented in the next subsection.

### 3.4 Quantum statistics. Identical particles

In practical cases, we are interested in identical particles, for instance, electrons. Thus, the permutation statistical effects must be included into consideration. It means that the density matrix should be symmetrized (antisymmetrized) upon particles’ permutations for the cases of bosons (fermions). Historically, there appeared two approaches, which were developed under pure bead trajectory representation of Barker [6] and, therefore, we shall start their presentation from the pure bead case.

Within the first approach, the density matrix is presented as a symmetric (bosons) or antisymmetric (fermions) sum of density matrices for distinguishable particles over all possible permutations [2, 47]:

\[ \rho^{(A,S)}(x_1^{(1)} \ldots x_1^{(N)} | x_{n+1}^{(1)} \ldots x_{n+1}^{(N)}) = \sum_{\{P\}} \frac{\gamma_P}{N!} \tilde{\rho}^{(D)}(x_1^{(1)} \ldots x_1^{(N)} | x_{n+1}^{(1)} \ldots x_{n+1}^{(N)}) \]  

(43)
where summation is taken over all permutations on $N$ particles, $\gamma = \pm 1$ for bosons and fermions, correspondingly, $[P]$ being the parity of the permutation $P$, and indices "$(A,S,D)$" stand for Antisymmetric, Symmetric and Distinguishable, respectively. The density matrix for distinguishable particles was considered in the previous section for the case of a single particle in one dimension. As it was already mentioned, its generalization to the case of $N$ particles in $d$ dimensions is straightforward, resulting in:

$$\rho^{(D)}(r_1^{(1)}, \ldots, r_{N}^{(N)}|r_{n+1}^{(1)}, \ldots, r_{n+1}^{(N)}) = \left(\frac{mn}{2\beta\hbar^2}\right)^{\frac{dN}{2}} \exp\left[\sum_{j=1}^{n} \left\{ \frac{mn}{2\beta\hbar^2} \sum_{i=1}^{N} (r_{j+1}^{(i)} - r_j^{(i)})^2 + \frac{\beta}{n} V \left(\{r_j^{(i)}\}\right) \right\} \right]$$

where $r_j^{(i)}$ is a $d$-dimensional vector, pointing bead number $j$ belonging to the particle $i$; $V \left(\{r_j^{(i)}\}\right)$ is the potential energy of the $j$-th time slice of all $N$ particles, or in other words, the potential energy of all beads, having index $j$. Note, that beads with different imaginary time or index $j$ do not have the potential interaction. Note also, that we consider only spinless particles here. A method accounting spin can be found elsewhere [89].

The partition function being the trace of the density matrix can be written as:

$$Z^{(A,S)}(\beta) = \frac{1}{N!} \sum_{\gamma} \gamma^{[P]} \int \left(\prod_{i=1}^{N} dr_i^{(i)}\right) \rho^{(D)}(r_1^{(1)}, \ldots, r_{N}^{(N)}|r_{n+1}^{(1)}, \ldots, r_{n+1}^{(N)})$$

under condition $r_1^{(i)} = r_{n+1}^{(i)}$. The latter requirement means that the end of trajectory of $i$-th particle is linked to the beginning of trajectory of another, permuted, $P(i)$-th particle. Note, that linked trajectories can be considered as ring ones, with length divisible by $n$. Interestingly, for noninteracting particles they may be interpreted as a single particle at a set of inverse temperatures: $\beta, 2\beta, 3\beta \ldots$ as it was shown in Paper I (see Sec. 5.6 and, particularly, Eq. (171)) for discussion).

The corresponding approach within Bead-Fourier scheme can be developed without any significant complications. One can also transform the sum over permutations to sum over classes of permutations in order to decrease the number of terms [90]. According to the partition function (45) exchange affects only the first and the last beads of each trajectory (particle). It was found possible to symmetrize the resulting equation in order to spread the exchange along the trajectory. For details, see Ref. [64].
In the other approach introduced by Takahashi and Imada [46] in 1984, the Trotter expansion acts on already (anti)symmetrized density matrix $\tilde{\rho}^{(A,S)}$, while antisymmetrization operation (43) is applied to each high-temperature density matrix in Trotter expansion. We start from the case of Fermi-Dirac statistics (fermions):

$$Z^{(A)} = \prod_{j=1}^{n} \prod_{\ell=1}^{N} \rho_j^{(A)}(r_j^{(1)}, \ldots, r_j^{(N)} | r_{j+1}^{(1)}, \ldots, r_{j+1}^{(N)})$$  \hspace{1cm} (46)$$

Each high-temperature antisymmetric density matrix $\rho_j^{(A)}$ is, in turn, presented as a sum over permutations of high-temperature density matrices for distinguishable particles:

$$\rho_j^{(A)}(r_j^{(1)}, \ldots, r_j^{(N)} | r_{j+1}^{(1)}, \ldots, r_{j+1}^{(N)}) = \frac{1}{N!} \left( \frac{mn}{2\pi \beta \hbar^2} \right)^{N/2} \times$$

$$\sum_{\gamma} \left[ \exp \left( -\frac{mn}{2\beta \hbar^2} \sum_{i=1}^{N} (r_i^{(1)} - r_i^{(N)})^2 - \frac{\beta}{2n} [V(\{r_i^{(1)}\}) + V(\{r_i^{(N)}\})] \right) \times$$

$$\det \left| \begin{array}{cccc}
\exp \left[ -\frac{mn}{2\beta \hbar^2} (r_1^{(1)} - r_i^{(1)})^2 \right] & \cdots & \exp \left[ -\frac{mn}{2\beta \hbar^2} (r_1^{(1)} - r_i^{(N)})^2 \right] \\
\vdots & \ddots & \vdots \\
\exp \left[ -\frac{mn}{2\beta \hbar^2} (r_N^{(1)} - r_i^{(1)})^2 \right] & \cdots & \exp \left[ -\frac{mn}{2\beta \hbar^2} (r_N^{(1)} - r_i^{(N)})^2 \right]
\end{array} \right|$$  \hspace{1cm} (47)$$

with boundary conditions $r_1^{(i)} = r_{n+1}^{(i)}$. In the case of bosons the determinant should be substituted with permanent, since $\gamma = 1$. Note, that potential energy terms do not enter the determinant, since in the pure bead representation potential energy is symmetric with respect to the particles’ permutations. Moreover, in this representation particles indeed become identical: due to the presence of determinants (permanents) any permutation of beads at some imaginary time does not change the total density matrix. Formulas, corresponding to the Bead-Fourier case will be considered in Sec. 5.1.

Note, that although these two approaches represent the same density matrix, the microscopic pictures are completely different. In the latter approach partial cancellation of positive and negative weights take place at each time slice $j$ and all permutations are considered simultaneously, while in the former all permutations are considered independently. Mathematically, the difference is in the order of operations, namely, Trotter expansion and summation over permutations. It was shown [46], that the latter approach is beneficial.
3.5 Thermodynamics and expectation values in terms of Path Integrals. Energy estimators.

Consider operator $\hat{O}$ which corresponds to an observable and assume that it is purely a function of coordinates: $\hat{O} = \hat{O}(x)$. By definition, the expectation value of $\hat{O}$ reads:

$$
\langle \hat{O} \rangle = \frac{\text{Tr} \left[ \hat{O} \exp \left( -\beta \hat{H} \right) \right]}{\text{Tr} \left[ \exp \left( -\beta \hat{H} \right) \right]} = \frac{1}{Z(\beta)} \text{Tr} \left[ \hat{O} \exp \left( -\beta \hat{H} \right) \right] \tag{48}
$$

Carrying out the trace in the coordinate basis gives:

$$
\langle \hat{O} \rangle = \frac{1}{Z(\beta)} \int dx \langle x | \hat{O} \exp \left( -\beta \hat{H} \right) | x \rangle = \frac{1}{Z(\beta)} \int dx o(x) \langle x | \exp \left( -\beta \hat{H} \right) | x \rangle \tag{49}
$$

where $o(x)$ is the corresponding eigenvalue of operator $\hat{O}$, obtained by acting on a coordinate eigenstate. Analogously, the expression for the expectation value of operator $\hat{O}$ can be presented as a continuous path integral of the form:

$$
\langle \hat{O} \rangle = \frac{1}{Z(\beta)} \int Ds \, o[s] \exp \left( -\frac{1}{\hbar} S[x(s)] \right) \tag{50}
$$

It can also be written as a limit of a discrete path integral:

$$
\langle \hat{O} \rangle = \frac{1}{Z(\beta)} \lim_{n \to \infty} \int dx_1 \ldots dx_n o(x_1) \exp \left[ -\beta U_{\text{eff}}(x_1, \ldots, x_n) \right] \tag{51}
$$

under cyclic condition: $x_{n+1} = x_1$. Since the integral in (51) is invariant under a cyclic relabeling of all PI variables, i.e., $x_1 \to x_2, x_2 \to x_3, \ldots$, such a relabeling can be done $n$ times, the resulted expressions summed together and divided by $n$ yielding:

$$
\langle \hat{O} \rangle = \frac{1}{Z(\beta)} \lim_{n \to \infty} \int dx_1 \ldots dx_n \frac{1}{n} \sum_{i=1}^{n} o(x_i) \exp \left[ -\beta U_{\text{eff}}(x_1, \ldots, x_n) \right] \tag{52}
$$

A finite $n$ expression can be obtained by substituting $Z(\beta)$ by $Z_n(\beta)$ (33) and removing the limit:

$$
\langle \hat{O}_n \rangle = \frac{1}{Z_n(\beta)} \int dx_1 \ldots dx_n o_n(x_1, \ldots, x_n) \exp \left[ -\beta U_{\text{eff}}(x_1, \ldots, x_n) \right] \tag{53}
$$
where \( o_n(x_1, \ldots, x_n) \):

\[
o_n(x_1, \ldots, x_n) \equiv \frac{1}{n} \sum_{i=1}^{n} o(x_i) \quad (54)
\]
is called an estimator for the operator \( \hat{O} \). In the limit \( n \to \infty \), the average of \( o_n(x_1, \ldots, x_n) \) with respect to a probability distribution function \( f_n \), \( f_n \equiv \exp [-\beta U_{eff}(x_1, \ldots, x_n)] \) will yield the true expectation value of \( \hat{O} \):

\[
\langle \hat{O} \rangle = \lim_{n \to \infty} \langle o_n(x_1, \ldots, x_n) \rangle_{f_n} \quad (55)
\]

Estimators play an important role in PI simulations. Any observable quantity has a corresponding estimator, i.e., a function of the generalized coordinates, whose average gives the true expectation value of that observable, in the limit \( n \to \infty \). Estimators for thermodynamic quantities can be derived often, as derivatives of the partition function. Consider, e.g., total internal energy \( E \). According to the Gibbs-Helmholtz equation:

\[
E = -\frac{\partial}{\partial \beta} \ln Z(\beta) = -\frac{1}{Z(\beta)} \frac{\partial Z(\beta)}{\partial \beta} \quad (56)
\]

The internal energy estimator \( \epsilon_n(x_1, \ldots, x_n) \) is obtained by substituting \( Z_n(\beta) \) for the true \( Z(\beta) \) and computing the derivative required. It is easy to demonstrate that

\[
\epsilon_n(x_1, \ldots, x_n) = \frac{n}{2\beta} - \sum_{i=1}^{n} \frac{mn}{2\beta^2 h^2} (x_{i+1} - x_i)^2 + \frac{1}{n} \sum_{i=1}^{n} \phi(x_i) \quad (57)
\]

\( \epsilon_n(x_1, \ldots, x_n) \) in Eq. (57) is known as the primitive energy estimator. The last sum in Eq. (57) is easily recognized as the potential energy estimator, while the rest refers to the kinetic part. Notice, that the kinetic energy estimator is the difference of two large numbers when \( n \) is big, and as Herman, Bruskin and Berne [53] showed, its statistical error grows with \( n \). These authors derived an equivalent form of the estimator based on the virial theorem:

\[
\epsilon_n^{vir}(x_1, \ldots, x_n) = \frac{1}{2n} \sum_{i=1}^{n} x_i \frac{\partial \phi(x_i)}{\partial x_i} + \frac{1}{n} \sum_{i=1}^{n} \phi(x_i) \quad (58)
\]

This alternative form of the total energy estimator is usually referred as virial estimator.

Just to mention, other thermodynamics estimators were derived, e.g., for pressure [91], heat capacity [92], magnetic susceptibility [4]. Estimators in case of identical particles and/or Bead-Fourier schemes can be obtained in the similar manner [64].
4 Molecular Dynamics

4.1 Fundamentals of classical mechanics.

In this section we briefly summarize the main concepts of the classical mechanics. The goal is to introduce its terms and ideas used in the thesis in a consequent manner.

Let a three-dimensional system contain \( N \) particles. Then, for this system, the number of degrees of freedom is \( 3N \). Any set of \( 3N \) values, that completely describes the positions of all the particles in the system is usually referred as generalized coordinates \( q_i \) and form the, so-called, configurational space. The time derivatives of the generalized coordinates are called generalized velocities and denoted \( \dot{q}_i \). If one knows both generalized coordinates and velocities at the same time, then one can predict the system evolution in time precisely. One often says, that classical mechanical equations of motion are deterministic, i.e., fully determined by the initial conditions.

The mechanical motion of any system is driven by the least action principle. According to it, the system is characterized by the function, called Lagrangian \( L(q_i(t), \dot{q}_i(t), t) \) and moves between time moments \( t_1 \) and \( t_2 \) so, that its action \( S \):

\[
S = \int_{t_1}^{t_2} dt L(q_i(t), \dot{q}_i(t), t)
\]

has an extremum (minimum). The least action principle leads to Euler-Lagrange equations:

\[
\frac{d}{dt} \frac{\partial L}{\partial \dot{q}_i} = \frac{\partial L}{\partial q_i}
\]

(60)

There exists an alternative formulation of classical dynamics, based on the Legendre transformed Lagrangian, called Hamiltonian:

\[
H \equiv p_i \dot{q}_i - L(q_i, \dot{q}_i, t)
\]

(61)

The value of the Hamiltonian (61) at any time is equal to the energy of the system:

\[
H = \sum_{i=1}^{3N} \frac{p_i^2}{2m} + \phi\{q_i\}
\]

(62)

where \( \phi\{q_i\} \) is the potential energy. Its natural variables are generalized momenta \( p_i \) instead of generalized velocities \( \dot{q}_i \), defined as:

\[
p_i \equiv \frac{\partial L}{\partial \dot{q}_i}
\]

(63)
The $6N$-dimensional space $\{p_i, q_i\}$ is called the phase space.

In order to derive Hamiltonian equations of motion, one has to express the Lagrangian from Eq. (61), substitute it into the definition of action (59) and apply the least action principle, resulting in:

$$
p_i = -\frac{\partial H}{\partial q_i}; \quad q_i = \frac{\partial H}{\partial p_i}
$$

(64)

$6N$ first-order differential equations (64) are called Hamiltonian equations of motion. In contrast, the Lagrangian formalism provides us with $3N$ second-order equations. Obviously, the general solution of either Euler-Lagrange or Hamiltonian equations will contain $6N$ parameters. Thus, $6N$ generalized coordinates and momenta provide the unique solution. However, both formalisms yield identical results, since Hamiltonian equations of motion (64) agree with Euler-Lagrange equations (60) via (61) and (63), as can easily be verified. The choice between the two is dictated by considerations of mathematical convenience.

It is easy to prove, that if the Hamiltonian (or Lagrangian) does not depend on time explicitly, which is the case, e.g., in closed systems, then the energy conserves.

Newton’s equations can be obtained directly from both the Hamiltonian and Lagrange formalisms. Consider, for instance, Hamiltonian equations of motion (64) in Cartesian coordinates:

$$
p_{x_i} = -\frac{\partial H}{\partial x_i} = -\frac{\partial \phi(\{x_i\})}{\partial x_i}
$$

$$
q_i = \frac{\partial H}{\partial p_{x_i}} = \frac{p_{x_i}}{m}
$$

(65)

The derivation of the Newton’s equations from the Lagrangian formalism can be carried out in the similar manner.

It is instructive to consider, so-called, canonical transformations. Since in the Hamiltonian formulation the generalized coordinates and momenta are independent variables, one can introduce the transformation of both variables simultaneously:

$$
Q_i = Q_i(q_i, p_i)
$$

$$
P_i = P_i(q_i, p_i)
$$

(66)

The transformation is called canonical, if the Hamiltonian equations of motion preserve the form (64) in new variables $\{Q_i, P_i\}$. 
Let $\eta$ be a $2N$-dimensional vector, containing $\{q_i,p_i\}$.\(^5\) Eqs. (64) can be written in a single equation, by using a matrix notation:

$$\dot{\eta}_i = -\omega \frac{\partial H}{\partial \eta_i} \quad (67)$$

where $\omega$ is an antisymmetric matrix defined as:

$$\omega \equiv \begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix} \quad (68)$$

In a similar way $2N$-dimensional vector $\xi$ can be defined, containing the transformed generalized coordinates and momenta $\{Q_i,P_i\}$. Let $J$ be the Jacobian of the transformation $\eta \to \xi$:

$$J_{ij} = \frac{\partial \xi_i}{\partial \eta_j} \quad (69)$$

It is possible to prove, that if $\eta \to \xi$ is a canonical transformation, then the Jacobian $J$ must satisfy the following criteria:

$$J\omega J^T = \omega \quad (70)$$

where $J^T$ is the transposed matrix of $J$. Eq. (70) is often called symplectic condition and $J$ - symplectic matrix.

Note, that the evolution of the system in time, according to the Hamiltonian equations of motion, can be considered as a canonical transformation of coordinates. Thus, we can conclude, that symplecticness is the natural property of the evolution of a Hamiltonian system in time. The latter fact is intensively exploited for creation of the MD integrators, discussed in the next subsection.

### 4.2 Numerical integration of equations of motion

Various algorithms have been designed for numerical integration of the Newton’s (Hamiltonian) equations of motion. The most naive one is based simply on a truncated Taylor expansion of the particle coordinates:

$$v(t + \Delta t) = v(t) + \frac{f(t)}{m} \Delta t$$

$$x(t + \Delta t) = x(t) + v(t) \Delta t + \frac{f(t)}{2m} \Delta t^2 \quad (71)$$

\(^5\)For the sake of simplicity, we consider a one-dimensional system.
Numerical integration of equations of motion

where \( f(x) \) is the force, \( v(x) \) being the velocity. The integration performed according to Eqs. (71) is known as **Euler** algorithm.

One of the simplest and, surprisingly, one of the best and, hence, popular algorithms is the, so-called, **Verlet** algorithm [93]. To derive it, we start from the Taylor’s expansion of the particle’s coordinate around time \( t \):

\[
x(t + \Delta t) = x(t) + v(t)\Delta t + \frac{f(t)}{2m}\Delta t^2 + \frac{\Delta t^3}{3!} \dddot{x} + O(\Delta t^4) \tag{72}
\]

similarly,

\[
x(t - \Delta t) = x(t) - v(t)\Delta t + \frac{f(t)}{2m}\Delta t^2 - \frac{\Delta t^3}{3!} \dddot{x} + O(\Delta t^4) \tag{73}
\]

Summing Eqs. (72) and (73) and truncating the result after the third order term results in:

\[
x(t + \Delta t) = 2x(t) - x(t - \Delta t) + \frac{f(t)}{m}\Delta t^2 \tag{74}
\]

The estimate of the new position contains an error that is of order \( \Delta t^4 \), where \( \Delta t \) is the time step of the MD scheme. Note, that velocities are not required in the algorithm. However, one can obtain them from the knowledge of the trajectory, using

\[
v(t) = \frac{x(t + \Delta t) - x(t - \Delta t)}{2\Delta t} + O(\Delta t^2) \tag{75}
\]

while knowledge of forces allows to reconstruct velocity \( v(t) \) with \( O(\Delta t^3) \) precision. Several algorithms are equivalent to the standard Verlet scheme (74). So-called, **velocity Verlet** method [94] has the same equation for the coordinates, as Euler one (71), but velocities are obtained as follows:

\[
v(t + \Delta t) = v(t) + \frac{f(t + \Delta t) + f(t)}{2m}\Delta t \tag{76}
\]

Note, that new velocities can be computed only after the new positions and, from these, new forces are obtained.

I would like to present one more Verlet-like integrator, named **Leap Frog**, since the PIMD program developed uses it. The algorithm evaluates the velocities at half-integer time steps and uses them to compute the new positions at integer time steps:

\[
\begin{align*}
v(t + \Delta t/2) &= v(t - \Delta t/2) + \frac{f(t)}{m}\Delta t \\
x(t + \Delta t) &= x(t) + v(t + \Delta t/2)\Delta t
\end{align*} \tag{77}
\]
It is possible to construct algorithms, which reproduce the exact molecular trajectories with a higher order of the time step $\Delta t$ than the Verlet algorithm. Here the predictor-corrector algorithm [95] is presented. Let us write down “predicted” positions, velocities, accelerations at time $t + \Delta t$ using Taylor expansion:

\[
\begin{align*}
    r^p(t + \Delta t) &= r(t) + \Delta tv(t) + \frac{1}{2}\Delta t^2 a(t) + \frac{1}{6}\Delta t^3 b(t) + \frac{1}{24}\Delta t^4 c(t) + \ldots \\
v^p(t + \Delta t) &= v(t) + \Delta ta(t) + \frac{1}{2}\Delta t^2 b(t) + \frac{1}{6}\Delta t^3 c(t) + \ldots \\
a^p(t + \Delta t) &= a(t) + \Delta tb(t) + \frac{1}{2}\Delta t^2 c(t) + \ldots \\
b^p(t + \Delta t) &= b(t) + \Delta tc(t) + \ldots
\end{align*}
\]

where $b(t)$ is the time derivative of acceleration $a(t)$, $c(t)$ is the time derivative of $b(t)$, and so on. Suppose also that we know all the functions $r(t)$, $v(t)$, $a(t)$, $b(t)$, $c(t)$, ... at the moment of time $t$, where accelerations $a(t)$ are defined by the forces calculated from the positions $r(t)$. Then we can compute “predicted” values of these functions according to Eqs. (78). Next, we compute new forces according to the predicted positions $r^p(t + \Delta t)$ and thus determine new accelerations $a(t + \Delta t)$. We also define “corrections” to the accelerations: $\Delta a \equiv a(t + \Delta t) - a^p(t + \Delta t)$

Then we can determine also corrections to other dynamical variables

\[
\begin{align*}
    r(t + \Delta t) &= r^p(t + \Delta t) + c_0\Delta t^2 \Delta a(t + \Delta t) \\
v(t + \Delta t) &= v^p(t + \Delta t) + c_1\Delta t \Delta a(t + \Delta t) \\
a(t + \Delta t) &= a^p(t + \Delta t) + c_2\Delta a(t + \Delta t) \\
b(t + \Delta t) &= b^p(t + \Delta t) + c_3\Delta a(t + \Delta t)/\Delta t \\
c(t + \Delta t) &= c^p(t + \Delta t) + c_4\Delta a(t + \Delta t)/\Delta t^2
\end{align*}
\]

The coefficients $c_i$ depend on the order of the method. For the third order the coefficients are: $c_0 = 1/6, c_1 = 5/6, c_2 = 1, c_3 = 1/3$ while for the forth order algorithm (which is given above) the coefficients are: $c_0 = 19/120, c_1 = 3/4, c_2 = 1, c_3 = 1/2, c_4 = 1/12$. After determination of the corrections (79), new forces must be calculated for the “prediction” part of the next step.

The predictor-corrector algorithm requires two calculations of forces at each step. Since forces’ calculations take most of the computer time in practically any simulation, the predictor-corrector algorithm is computationally equally expensive as the Verlet algorithm with twice shorter time step. Since we want to compare different algorithms presented, the question arises: what are the criteria for “good” or “bad” integration method?
First, the true Hamiltonian dynamics conserves the energy. Since the time steps are finite, energy is not strictly conserved. However, the stability of the total energy is often considered as an important criteria of how good the integration algorithm is. Usually, high-order algorithms, e.g., predictor-corrector ones, described above, have noticeable energy drifts on large time scales. In contrary, Verlet-style algorithms have rather small long-term drifts.

As it was already mentioned in the previous section, equations of motion are time reversible and symplectic. Hence, the integration method should also have those properties. An important advantage of a time-reversible molecular dynamics algorithm is that the positions’ error term of the order of $\Delta t^3$ disappears (since this term is not time-reversible), so only errors of the order $\Delta t^4$ remain. On the one hand, this improves the accuracy of MD trajectories’ calculation. On the other hand, it may allow longer time steps with maintaining the same accuracy. Using the non-time-reversible algorithms, apart of stronger deviations from “exact” trajectories, may bring additional problems. Particles spend most of the time in a vicinity of the potential energy minimum, where the second derivative of the potential is typically negative. The consequence is that numerical integration by a non-time-reversible algorithm causes systematic accumulation of errors, which may lead even to deviations of thermodynamic averages. It is quite easy to verify, that Euler algorithm, as well as predictor-corrector ones, are not time-reversible, while Verlet-style ones are.

One of the consequences of the symplectic property is the phase volume conservation. Although, the argument about preserving of the phase space volume sounds more philosophic than practical, the absence of this property may have direct practical consequences. Consider a non-area-preserving algorithm, mapping a volume $\Omega$ in the phase space on another (usually larger) volume $\Omega'$. After sufficiently long times one can expect the expansion of $\Omega'$ in the phase space, which is not compatible with the energy conservation. Indeed, as it was already mentioned, predictor-corrector algorithms have noticeable energy drifts.

In 1992 Tuckerman et al. [96] have shown how to derive time-reversible, area-preserving algorithms systematically, from the Liouville formulation of classical mechanics. Consider the system of $N$ particles in three dimensions, described by a set of generalized coordinates $\{q_i\}$ with conjugated generalized momenta $\{p_i\}$. The Liouville operator $L$ is defined as follows:

$$iL = \sum_{i=1}^{3N} \left[ \dot{q}_i \frac{\partial}{\partial q_i} + f_i \frac{\partial}{\partial p_i} \right]$$

(79)

where $f_i$ is the force, acting on the $i$th particle. Consider the instantaneous state of the system $\Gamma = \{q_i, p_i\}$. The classical propagator is then $U(t) = \exp(iLt)$. Then, for the evolution of a state in time one can write:
$$\Gamma(t) = U(t)\Gamma(0)$$  \hfill (80)

It is important to mention that $U(t)$ is a unitary operator, i.e., $U(-t) = U^{-1}(t)$. Eq. (80) is not very useful in the practical sense, since the evaluation of its right hand side is equivalent to the exact integration of the equations of motion. Our goal is to define a finite-time scheme, in which the state of the system $\Gamma$ will be propagated by small, but finite time shifts. However, in a few special cases the formal solution of Eq. (80) is known explicitly. In particular, if we split the Liouville operator (79) into coordinate and momenta parts:

$$iL = iL_q + iL_p \equiv \sum_{i=1}^{3N} \dot{q_i} \frac{\partial}{\partial q_i} + \sum_{i=1}^{3N} f_i \frac{\partial}{\partial p_i} \hfill (81)$$

and set $L$ to be equal $L_q$, then the propagation by $\exp(iL_q t)$ will result in a simple shift of coordinates according to:

$$\Gamma(t) = \Gamma(\{q_i(0) + \dot{q_i}(0)t, p_i(0)\})$$  \hfill (82)

Analogously, setting $L = L_p$ will result in a simple shift of momenta. Unfortunately, operators $L_q$ and $L_p$ do not commute and, therefore $\exp(iLt) \neq \exp(iL_q t) \times \exp(iL_p t)$. The solution is to use the Trotter theorem (4):

$$\exp[i(L_q + L_p)t] = \exp[i(L_q + L_p)t/P]^P \approx \exp[iL_p\Delta t/2] \exp[iL_q\Delta t] \exp[iL_p\Delta t/2] \equiv G(\Delta t)$$  \hfill (83)

where $\Delta t \equiv t/P$. In the matter of fact, we achieved what we set out to do: $G(\Delta t)$ is the finite-time classical propagator. I would like to emphasize, that since the classical propagator $U(t)$ is unitary, as well as all three factors in $G(\Delta t)$, it is easy to show, that $G(\Delta t)$ is unitary itself. This means, that any integrator, based on this Trotter factorization will be both time-reversible and phase space volume preserving!

As an example, it is easy to demonstrate, that acting on the initial state $\Gamma(\{q_i(0), p_i(0)\})$ with $G(\Delta t)$ one will ultimately get equations for velocity Verlet [94] algorithm.

Not going into details, I would like to mention, that Trotter expansion carried out up to higher order [58] will yield higher order integrators. Note also, that the Liouville operator can be split in more than two parts (for instance, fast and slow motions can be also separated), providing a route to multiple time scale reversible algorithms [96]. Also, this formalism allows to incorporate a thermostat into the integrator in a time-reversible manner (see, e.g. [97]).
In conclusion, I would like to discuss briefly the important feature of MD trajectories, named **Lyapunov instability**. Not going into details, it can be formulated as: Any, even very small difference in the initial conditions, leads to an exponential divergence of the MD trajectories with time. In other words, system “forgets” about the initial conditions very fast. Although the equations of motion are time-reversible, if we, e.g., change the signs of all momenta, the system would not return to the initial point, due to round-off errors. It may seem counterintuitive, but just the fact of the trajectories’ instability is essential for obtaining correct thermodynamical averages via MD. In statistical thermodynamics, the basic assumption is that all states of the same energy are equally probable. Due to the Lyapunov instability, the time evolution of the system in the phase space acquires more and more features of stochastic, random motion, with the only limitation that the total energy is constant. As a result, there occurs a probability distribution, which corresponds to the microcanonical ensemble. Methods to deal with the canonical ensemble are described in the next subsection.

### 4.3 Molecular dynamics at constant temperature. Thermostats

Molecular dynamics, being the numerical solution of Newton’s equations with conserved total energy, naturally corresponds to the microcanonical ensemble. Since we are interested in constant temperature, i.e., the canonical ensemble, we should provide a way to keep the temperature constant.

An important question to answer before considering different schemes to perform MD at constant temperature is: what is meant by constant temperature? From the statistical mechanical point of view there is no ambiguity: we can impose a temperature on a system by bringing it into a thermal contact with a large heat bath. Thus, the probability of finding the classical system in a given energy state is determined by the Maxwell-Boltzmann distribution (the expression is written for one particle in three dimensions):

\[
\mathcal{P}(p) = \left( \frac{1}{2\pi mk_B T} \right)^{3/2} \exp \left[ -\frac{p^2}{2mk_B T} \right]
\]

Ultimately we obtain a simple relation known as **equipartition theorem**:

\[
\left\langle \frac{p^2}{2m} \right\rangle = \frac{1}{2} k_B T
\]

where \(m\) is the particle mass, \(T\) is the temperature, \(k_B\) is the Boltzmann constant, \(p\) and \(p_\alpha\) being the momentum and its \(\alpha\) component. In other words, the average kinetic energy of each degree of freedom is constant equal to \(k_B T/2\).
The most obvious and trivial idea to satisfy the criteria (85) is to set the total kinetic energy of the system to constant.\(^6\)

\[
\sum_{i=1}^{N} \frac{p_i^2}{2m_i} = \frac{3N}{2} k_B T \tag{86}
\]

The simplest and naive way to do so is to scale velocities (momenta) on each MD step in order to preserve constraint (86):

\[
p_i \leftarrow p_i \cdot \left( \frac{3N k_B T}{\sum_{i=1}^{N} p_i^2 / m_i} \right)^{\frac{1}{2}}, \forall i \tag{87}
\]

This momenta scaling procedure has been invented by Woodcock [98] in an \textit{ad hoc} fashion and used without demonstrated justification. Broughton \textit{et al.} [99] were more cautious and applied the scaling at infrequent intervals only. Haile and Gupta [100] discussed how to add the constraint of constant kinetic energy to the equations of motion. As a special case they proposed a constraint method based on momenta scaling procedure. The principal drawback of the momenta scaling methods is, that providing correct average value of momenta (86), they do not generally satisfy the condition for the distribution of momenta (85). Thus, the canonical ensemble distribution is not guaranteed even for coordinates. Later, Nosé [101] demonstrated that the equilibrium distribution function in the momenta scaling method deviates from the canonical one by order \(N^{-\frac{1}{2}}\).

Hoover \textit{et al.} [102, 103] and simultaneously and independently Evans [104] proposed a constrained MD method, derived from a non-equilibrium MD formulation [105]. In this method an additional term is added to the force term:

\[
\frac{dp_i}{dt} = -\frac{\partial H}{\partial q_i} - \alpha p_i \tag{88}
\]

The parameter \(\alpha\) is determined from the requirement that total kinetic energy is constant:

\[
\sum_{i=1}^{N} \frac{p_i^2}{2m_i} = \frac{1}{2} g k_B T \Rightarrow \frac{1}{m_i} \sum_{i=1}^{N} p_i \frac{dp_i}{dt} = 0 \tag{89}
\]

Thus, we get:

\[
\alpha = \frac{\sum_{i=1}^{N} \frac{p_i}{m_i} \frac{\partial H}{\partial q_i}}{\sum_{i=1}^{N} \frac{p_i}{m_i}} \tag{90}
\]

\(^6\)From here we consider \(N\) particles in three dimensions.
This method, referred as isokinetic ensemble, can produce the canonical distribution in the coordinate space if we set \( g \equiv 3N - 1 \) (\( g = 3N \) in the original papers [102, 104]). Twenty years later it was reconsidered by Minary, Martyna and Tuckerman [106, 107] for biophysical, PI and \textit{ab initio} molecular dynamics. They claimed that “the constraint approach has not been as widely adopted as the extended system technique because the full power of the former has not yet been fully realized”. Although, the variance in the kinetic energy in the canonical ensemble is non-zero, which can be easily verified (see, e.g. [108]), it is zero by construction in the isokinetic ensemble method. Thus, the latter formally does not correspond to the canonical ensemble. In practice, the difference between isokinetic and canonical schemes is often negligible. In other words, the isokinetic scheme is well behaved in the sense that it yields the correct canonical averages for all properties that depend on particles’ positions only. Indeed, the partition function of the isokinetic ensemble reads as follows:

\[
Q(N, V, T) \propto \prod_{i=1}^{N} (dp_i dr_i) \delta \left( \sum_{i=1}^{N} \frac{p_i^2}{2m_i} - \frac{dN - 1}{2} k_B T \right) \exp \left[ -\beta \phi (r_1, \ldots, r_N) \right]
\]

(91)

here some normalizing constants are omitted. Clearly, the partition function is separable and

\[
Q(N, V, T) \propto Z(N, V, T) = \prod_{i=1}^{N} (dr_i) \exp \left[ -\beta \phi (r_1, \ldots, r_N) \right]
\]

(92)

Thus, the configurational integral of the isokinetic ensemble \( Z(N, V, T) \) coincides with that of the standard canonical ensemble, providing all position-dependent equilibrium properties of two ensembles to be equal, as it was declared above.

Probably one the most famous pioneer works has been done by Andersen [87], in which he proposed thermostats for constant pressure and/or temperature. In contrary to the pressure thermostat, which was developed by introducing the additional artificial degree of freedom (so-called, extended Lagrangian approach), the temperature one was a hybrid of MD and MC methods. The idea was to couple a system to a heat bath that imposes the desired temperature. Namely, randomly selected particles change their velocities by stochastic collisions, which occur occasionally. These collisions can be considered as MC moves from one constant energy shell to another, since the system evolves according to Newtonian laws in-between. The distribution of the collided particles velocities is chosen to reproduce the canonical ensemble. The time probability distribution between two successive collisions has the Poisson form:
\[
\mathcal{P}(t; \nu) = \nu \exp [-\nu t]
\]  

(93)

where \( \nu \) is the predefined parameter, having the sense of the collisions frequency. One can say, that \( \nu \) determines the coupling strength to the heat bath. Mixing MD with stochastic collisions turns it into a Markov process. Andersen stated, that "...the time average of any \( F \) calculated from this trajectory is equal to the ensemble average of \( F \) for the canonical ensemble...". One of the lacks of the Andersen thermostat is, that it does not preserve momentum conservation. Later, Lowe [109] introduced a thermostat based on the ideas of the Andersen one, in which particles collides not with a thermal bath, but with each other, while the momentum is conserved by the construction of those collisions.

Andersen himself [87] failed to develop the extended Lagrangian method for the constant temperature MD, although he suggested that it might be possible. Indeed, Nose [101, 110] developed such a scheme. Consider a physical system of \( N \) particles described by coordinates \( \mathbf{r}_1, \ldots, \mathbf{r}_N \) in the volume \( V \) interacting via potential energy \( \phi(\mathbf{r}_1, \ldots, \mathbf{r}_N) \). An additional degree of freedom \( s \) is introduced, which acts as an external system. The interaction between the physical system and \( s \) is expressed via the velocity scaling (one can also consider it as a time scaling):

\[
\mathbf{v}_i \equiv s \mathbf{f}_i
\]  

(94)

\( \mathbf{v}_i \) is the "real" velocity of the \( i \)-th particle. Thus, the extended Lagrangian is postulated to be:

\[
\mathcal{L}_{\text{Nose}} \equiv \sum_{i=1}^{N} \frac{m_i}{2} s^2 \dot{r}_i^2 - \phi(\{\mathbf{r}_i\}) + \frac{Q s^2}{2} - \frac{f}{\beta} \ln s
\]  

(95)

where \( f \) is the parameter that will be fixed later. \( Q \) is an effective mass associated with \( s \), while \( Qs^2/2 \) is the corresponding kinetic term. Note, that \( Q \) does not have dimensions of mass, but has the dimension of \( \text{energy} \times \text{time}^2 \) and determines the time scale of the temperature fluctuation. The equations of motion for coordinates \( \mathbf{r}_i \) and \( s \) are immediately derived from Lagrangian equations (see Sec. 4.1):

\[
\mathbf{p}_i \equiv \frac{\partial \mathcal{L}_{\text{Nose}}}{\partial \dot{\mathbf{r}}_i} = m_i s^2 \dot{r}_i^2 \quad p_s \equiv \frac{\partial \mathcal{L}_{\text{Nose}}}{\partial \dot{s}} = Q \dot{s}
\]  

(96)

Thus, the extended Hamiltonian reads:

\[\text{Author means the trajectory in the phase space obtained by the described above hybrid of MC and MD.}\]
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\[ \mathcal{H}_{\text{Nose}} = \sum_{i=1}^{N} \frac{p_i^2}{2m_i} + \phi (\{r_i\}) + \frac{p_s^2}{2Q} + \frac{f}{\beta} \ln s \]  

(97)

The extended system generates the microcanonical ensemble of \(6N+2\) degrees of freedom, with the partition function:

\[ \mathcal{Q}_{\text{Nose}} = \frac{1}{N!} \int dp_s ds \prod_{i=1}^{N} (dp_i dr_i) \delta (E - \mathcal{H}_{\text{Nose}}) \]  

(98)

where we implicitly assumed, that energy conservation is the only conservation law. Following Nosé we introduce real variables (denoted by prime) which refer to virtual ones by:

\[ p'_i \equiv \frac{p_i}{s}, \quad r'_i \equiv r_i, \quad \Delta t' = \frac{\Delta t}{s} \]  

(99)

Note, that real time step fluctuates during the simulation. Let us also define the shortened form of the Hamiltonian, that corresponds to “physical” degrees of freedom:

\[ \mathcal{H} = \sum_{i=1}^{N} \frac{p_i'^2}{2m_i} + \phi (\{r_i'\}) \]  

(100)

Using the property of \(\delta\)-function:

\[ \delta [h (s)] = \frac{\delta (s - s_0)}{h' (s)} \]  

(101)

where \(s_0\) is a root of function \(h (s)\), we find for the partition function:

\[ \mathcal{Q}_{\text{Nose}} = \frac{1}{N!} \int dp_s ds \prod_{i=1}^{N} (dp_i dr_i') \frac{\beta s^{3N+1}}{f} \delta \left( s - \exp \left[ -\frac{\beta}{f} \left( H + \frac{p_s^2}{2Q} - E \right) \right] \right) \]  

(102)

Performing the integration over \(s\) and \(p_s\) analytically we arrive at:

\[ \mathcal{Q}_{\text{Nose}} = \frac{C}{N!} \prod_{i=1}^{N} (dp_i dr_i') \exp \left[ -\frac{3N+1}{f} \beta H \right] \]  

(103)

Obviously, the partition function (103) will coincide with the partition function of the canonical ensemble, if we set \(f = 3N + 1\).

One can derive equations of motion for the virtual variables (\(p, r\) and \(t\)) from the Hamiltonian (97):
\[
\frac{d\mathbf{r}_i}{dt} = \frac{\partial H_{\text{Nose}}}{\partial \mathbf{p}_i} = \frac{\mathbf{p}_i}{m_is^2} \tag{104}
\]
\[
\frac{d\mathbf{p}_i}{dt} = -\frac{\partial H_{\text{Nose}}}{\partial \mathbf{r}_i} = -\frac{\phi(\{\mathbf{r}_i\})}{\partial \mathbf{r}_i} \tag{105}
\]
\[
\frac{ds}{dt} = \frac{\partial H_{\text{Nose}}}{\partial p_s} = \frac{p_s}{Q} \tag{106}
\]
\[
\frac{dp_s}{dt} = -\frac{\partial H_{\text{Nose}}}{\partial s} = \frac{1}{s} \left( \sum_{i=1}^{N} \frac{p_{i}^2}{m_is^2} - \frac{f}{\beta} \right) \tag{107}
\]

Obviously, equations of motion can be written in terms of real variables, by combining (107) and (99). In a simulation it is not convenient to work with fluctuating time intervals, therefore the real-variable formulation is preferable. Hoover [111, 112] suggested to reformulate Nosé equations in order to avoid time scaling. He pointed out that variables \(s\) and \(p_s\) appear only as a product in the equations and thus he introduced a thermodynamic friction coefficient \(\xi \equiv s'p_s/Q\) and demonstrated that equations of motion transform into (primes are omitted and dots are used to denote real time derivatives):

\[
\dot{\mathbf{r}}_i = \frac{\mathbf{p}_i}{m_i} \tag{108}
\]
\[
\dot{\mathbf{p}}_i = -\frac{\phi(\{\mathbf{r}_i\})}{\partial \mathbf{r}_i} - \xi \mathbf{p}_i \tag{109}
\]
\[
\dot{\xi} = \frac{1}{Q} \left( \sum_{i=1}^{N} \frac{p_{i}^2}{m_is^2} - \frac{f}{\beta} \right) \tag{110}
\]
\[
\dot{s} = s\xi \tag{111}
\]

The first three equations form a closed set, so the last one is redundant. But it seems still useful to keep it, in order to track the conserved quantity of Nosé-Hoover scheme, i.e., as a diagnostics tool. In terms of variables used in (111) the conserved quantity looks like:

\[
H_{NH} = \sum_{i=1}^{N} \frac{p_{i}^2}{2m_i} + \phi(\{\mathbf{r}_i\}) + \frac{\xi^2 Q}{2} + \frac{f \ln s}{\beta} \tag{112}
\]

It seems important to underline that \(H_{NH}\) is not a Hamiltonian, although it is denoted with the same letter and has similar structure. The equations of motion can not be derived from it. Note also, that for any real variables formulation \(f = 3N\), not \(f = 3N + 1\) as for virtual variables one [101].
Molecular dynamics at constant temperature. Thermostats

Hoover [111] claimed, that the equations of motion (111) are unique in the sense that other equations of the same form can not lead to a canonical distribution. He also pointed the similarity of the equations with those of HLME constraint method [102, 103, 104, 105], as well as with those proposed by Berendsen [113]. The disadvantage of the latter is that the equations of motion appear to be non-reversible. Nosé [114] extended the method to include more than one temperature control variable. This extension makes it possible to control temperatures of different degrees of freedom separately, which can be useful, e.g., if they have different time scales.

The unexpected problem appeared when probably the simplest test system, the canonical harmonic oscillator has been studied. Posch, Hoover and Vesely [115] studied the one-dimensional Nosé harmonic oscillator and claimed, that: “The Nosé oscillator is a borderline case, not sufficiently chaotic for a fully statistical description. We suggest that the behaviour of only slightly more complicated systems is considerably simpler and in accord with statistical mechanics”. Hamilton [116] observed, that for harmonic oscillator canonical averages are dependent on the choice of the “thermostat mass” \( Q \), as well as on the initial conditions. In other words, the Nosé harmonic oscillator is not ergodic, while the ergodicity is the basement of the Nosé method. Hamilton [116] suggested to enforce the virial theorem in order to induce chaotic phase-space dynamics. This extension introduces a new degree of freedom in the system with an additional undefined parameter. Another possible extension of Nosé-Hoover approach by two degrees of freedom is discussed by Bulgac and Kusnezov [117]. They, as well as Jellinek [118] stated that there exists an infinite number of Nosé’s types of prescription in contrary to Hoover [111]. Jellinek and Berry [118, 119, 120] discussed the general way of extensions of Nosé-Hoover approach in details. Winkler [121] proposed a method with non-linear coupling to the thermal bath by only one parameter.

Anyhow, the breakthrough has been done by Martyna, Klein and Tuckerman [122] who developed the idea of Nosé-Hoover chains. They noticed, that “While the Gaussian fluctuations of momenta is driven with a thermostat, there is nothing to drive the fluctuations of the thermostat momentum”. Obviously, their idea was to introduce a second thermostat, that will thermostatate the first one, and so on. The equations for Nosé-Hoover chains can be found in [122]. Currently, Nosé-Hoover chains thermostat is probably the most used one.

It should be mentioned, that developing of advanced thermostats, as well as integrators nowadays, can be considered as a separate branch of science, with many scientific groups participating in this work (see, e.g., book [123]). The detailed description of their achievements is outside of the scope of this thesis.

I want to conclude this section, by mentioning the works of Tuckerman et al. [124, 125], in which authors has derived a rigorous classical statistical
4.4 Application to Path Integrals

Let us again consider the expression for the partition function (33). In order to derive the form suitable for MD we introduce the corresponding kinetic terms to each of the \( n \) particles and perform an integration over momenta conjugated to the beads coordinates \( x_j \):

\[
Z_n = \mathcal{N} \int d\mathbf{p}_1 \ldots d\mathbf{p}_n \cdot dx_1 \ldots dx_n \exp \left\{ -\beta \sum_{j=1}^{n} \frac{p_j^2}{2\tilde{m}_j} + U_{\text{eff}}(x_1, \ldots, x_n) \right\}
\]

(113)

Note, that the Gaussian integrals over momenta are uncoupled and can be performed analytically, and, thus, masses \( \tilde{m}_j \) can be chosen arbitrary, leading only to the appropriate choice of the normalization constant \( \mathcal{N} \). Formally, Eqs. (113) and (33) are equivalent, but the former will allow us to carry out molecular dynamics equations of motion, while the latter is sufficient only for Monte Carlo procedures.

In this section, we consider the pure bead scheme, while Bead-Fourier one would be discussed in Sec. 5.1. As we have demonstrated already, the effective potential \( U_{\text{eff}} \) under pure bead representation is (34):

\[
U_{\text{eff}}(x_1, \ldots, x_n) \equiv \sum_{j=1}^{n} \left[ \frac{m_{\omega}^2 n}{2}(x_{j+1} - x_j)^2 + \frac{1}{n} \phi(x_j) \right]
\]

(114)

The effective potential \( U_{\text{eff}} \) is treated as the potential energy, while the new Hamiltonian reads:

\[
H(x_1, \ldots, x_n; p_1, \ldots, p_n) = \sum_{j=1}^{n} \frac{p_j^2}{2\tilde{m}_j} + \frac{m_{\omega}^2 n}{2}(x_{j+1} - x_j)^2 + \frac{1}{n} \phi(x_j)
\]

(115)

Since we have connected the quantum partition function to a fictitious classical partition function, Eq. (113) can be evaluated, at least in principle, using classical MD based on equations of motion derived from (115). However, such a direct application of MD is problematic, as it was shown by Hall and Berne [71]. First, as the number of beads becomes large, springs between beads become stiff, since the effective force constant is proportional to the number of beads \( n \) (35). At the same time, the contribution from the potential is scaled by \( 1/n \) and, thus, the harmonic forces dominate. This causes MD trajectories to become similar with those, that correspond to the free particle (\( \phi = 0 \)), and
not explore the full available phase space. The latter means the presence of
ergodicity problem. Second, since the classical analogue of the quantum particle
cconsists of beads, connected with their neighbours by harmonic springs
(the second term in Eq. (115)), the characteristic frequencies of such a system
differ a lot in magnitude. Thus, the highest frequency of those, limits the
time step that can be used, causing a slow convergence of the static observ-
ables described mainly by lower frequency modes. Obviously, it leads in the
best case to a very inefficient simulation, and to an incorrect one in the worst.
Third, ordinary MD corresponds to a microcanonical ensemble, while we are
interested in the canonical properties. Thus, the proper thermostat should
be implemented. The solution to the latter problem is described in details in
Sec. 4.3.

Let’s consider the transformation of integration variables in Eq. (113) (and
the corresponding reconstruction of the Hamiltonian (115)) which serves to
uncouple the harmonic term and, thus, to solve the problem of efficiency. Historically, there appeared two variants of such a transformation. One is called staging and was initially developed for MC [47, 126]. Tuckerman et al. [72]
developed staging MD scheme. Consider a change of variables of the form:

\[ u_1 = x_1, \quad u_j = x_j - \frac{(j-1)x_{j+1} + x_1}{j} \quad (116) \]

This transformation is known as a staging transformation. Note, that the in-
verse transformation can be expressed in a simple recursive fashion:

\[ x_1 = u_1, \quad x_j = u_j + \frac{(j-1)x_{j+1} + u_1}{j} \quad (117) \]

where the term \( j = n \) is used to start the recursion. Performing staging trans-
formation (116) in Eq. (113) leads to the resulting equation for the partition
function:

\[ Z_n = \mathcal{N} \int dp_1 \ldots dp_n \int du_1 \ldots du_n \exp \left\{ -\beta \sum_{j=1}^n \frac{p_j^2}{2m_j} + U_{eff}(u_1, \ldots, u_n) \right\} \quad (118) \]

where the transformed effective potential is:

\[ U_{eff}^{stag}(u_1, \ldots, u_n) = \sum_{j=1}^n \frac{m_j \omega_0^2}{2} u_j^2 + \frac{1}{n} \phi(\{x_j(u_1, \ldots, u_n)\}) \quad (119) \]

Here, staging masses \( m_j \) are set as follows:
\[ m_1 = 0, \quad m_j = \frac{j}{j-1} m \quad (120) \]

Note, that the quadratic term in Eq. (119) is completely uncoupled in the terms of the staging coordinates \( u_j \), so the goal declared above is reached. Note also, that the variable \( u_1 \) does not appear in the transformed harmonic term, since \( m_1 = 0 \). This illustrates the well known fact, that \( n \) coupled oscillators can be presented as \( n - 1 \) uncoupled ones.

The corresponding staging Hamiltonian reads:

\[ H (u_1, \ldots, u_n; p_1, \ldots, p_n) = \sum_{j=1}^{n} \frac{p_j^2}{2\tilde{m}_j} + \frac{m_j \omega_j^2 u_j^2}{2} + \frac{1}{n} \phi (\{x_j (u_1, \ldots, u_n)\}) \quad (121) \]

The optimal choice of masses \( \tilde{m}_j \) is, obviously:

\[ \tilde{m}_1 = m, \quad \tilde{m}_j = m_j \quad (122) \]

since, with this choice all staging modes \( u_2, \ldots, u_n \) will move on the same time scale, thereby leading to efficient sampling of all modes in a MD scheme. I would like to underline, that the Hamiltonian (121) is neither not equivalent to the Hamiltonian (115), nor should it be! It generates a different dynamics, that sample the configuration space more effectively. The equations of motions, derived from Eq. (121) are:

\[ \dot{u}_j = \frac{p_j}{\tilde{m}_j} \]
\[ \dot{p}_j = -m_j \omega_j^2 u_j - \frac{\partial \phi}{\partial u_j} \quad (123) \]

The forces, \( \partial \phi / \partial u_j \) can also be retrieved in a recurrent manner:

\[ \frac{\partial \phi}{\partial u_1} = \sum_{j=1}^{n} \frac{\partial \phi}{\partial x_j} \]
\[ \frac{\partial \phi}{\partial u_j} = \frac{\partial \phi}{\partial x_j} + \frac{j-2}{j-1} \frac{\partial \phi}{\partial u_{j-1}} \quad (124) \]

This form is especially convenient, since the bead forces \( \partial \phi / \partial x_j \) can be computed directly, given the form of the potential, without any additional effort.

The other possible transformation, is the, so-called, normal mode transformation (see, e.g. \[78, 127\]) obtained by performing a Fourier expansion of the discrete cyclic path:
\[ x_j = \sum_{l=1}^{n} c_l \exp \left[ 2\pi i (j - 1)(l - 1)/n \right] \] (125)

The coefficients \( c_l \) are complex, so the normal mode variables, \( u_l \) are given by

\[ u_1 = c_1, \quad u_n = c_{n/2+1}, \quad u_{2l-2} = \text{Re}(c_l), \quad u_{2l-1} = \text{Im}(c_l) \] (126)

The corresponding set of normal mode frequencies:

\[ \lambda_{2l-1} = \lambda_{2l-2} = 2n \left[ 1 - \cos \left( \frac{2\pi (l - 1)}{n} \right) \right] \] (127)

from which a set of normal mode masses can be obtained, resulting in:

\[ m_l = m \cdot \lambda_l \] (128)

The PIMD equations (123) are equally valid for the normal mode transformation. The normal mode method has the advantage, that the mode \( u_1 \) is given, in terms of bead variables, by

\[ u_1 = \frac{1}{n} \sum_{j=1}^{n} x_j \] (129)

i.e., the path centroid. This can be beneficial, e.g., to perform approximate quantum dynamics via centroid MD approach, developed by Cao and Voth [73, 74, 75, 76]. The advantage of the staging transformation is that coordinate transformations \( u \to x, x \to u \), as well as forces transformation have simple recursive form.
5 Summary and discussion of the papers

5.1 Developing the Bead-Fourier molecular dynamics scheme

The derivation of the Bead-Fourier scheme was demonstrated in Sec. 3.2. Further development of the BF approach is presented below, using Eqs. (41) and (42) as a starting point. Those equations correspond to the case of Boltzmann statistics, i.e., distinguishable particles. Before passing to the case of identical particles, I would like to describe some problems of the direct application of BF scheme via molecular dynamics.

First, Eqs. (41) and (42) are suitable for MC, not for MD. Following the ideas, described in Sec. 4.4, we treat the Hamiltonian (42) as the potential energy and introduce corresponding kinetic terms. Then, the total BF Hamiltonian reads:

\[
H_{BF} = \sum_{i=1}^{N} \sum_{j=1}^{n} \left( \frac{p_{ij}^2}{2\tilde{m}_{ij}} + \sum_{k=1}^{m_{ij}} \frac{p_{ijk}^2}{2\tilde{m}_{ijk}} \right) + U_{c\ell}^{BF}(\{r_{ij}, a_{ijk}\})
\]

(130)

where \(U_{c\ell}^{BF}(\{r_{ij}, a_{ijk}\})\) coincides with the Hamiltonian from Eq. (42), generalized for the case of \(N\) particles and three dimensions. \(p_{ij}\) and \(p_{ijk}\) are the momenta, conjugated to \(r_{ij}\) and \(a_{ijk}\), respectively. The Hamiltonian \(H_{BF}\) can be used for derivation of Hamiltonian equations of motion according to Eq. (64), with both beads’ coordinates and Fourier amplitudes treated as generalized coordinates, with their momenta treated as generalized momenta. Thus, there would be \(6Nn(1 + k_{max})\) first-order differential equations. The details of the MD implementation are presented in Papers II, III.

Direct application of the scheme described above causes the problem of different time scales, which was pointed out in Sec. 4.4. Its first origin is the harmonic coupling of beads, exactly as in the pure bead case. The second is the prefactor \((k\pi)^2/2\) at the quadratic Fourier term \(a_{ijk}^2\). Although it is possible to use BFPIMD as is, i.e., ignoring this problem, as we have done in Papers II, III, it may be not very efficient and can lead to convergence problems in some cases. Hence, I suggest a recipe to avoid it and reformulate the BF scheme in order to make all degrees of freedom oscillate on the same time scale.

The harmonic coupling can be resolved exactly in the same manner, as in the pure bead case, by either staging or normal modes variable transformation (see Sec. 4.4 for details).\(^9\) Indeed, beads and Fourier amplitudes are coupled only by the potential energy term. Hence, we can consider Fourier amplitudes as parameters and perform exactly the same staging transformation \(u = u(x)\) as in the pure bead case (116), resulting in:

\(^{8}\)The formalism is written for \(N\) particles in three dimensions

\(^{9}\)Staging seems preferable, since the corresponding formulas have simple recursive form.
\[ U_{\text{eff}}^{BF}(\{u_{ij}, a_{ijk}\}) = \sum_{i=1}^{N} \sum_{j=1}^{n} \frac{\omega_{n}^2}{2} \left( m_{ij} u_{ij}^2 + m \sum_{k=1}^{k_{\text{max}}} \frac{(k\pi)^2}{2} a_{ijk}^2 \right) + \frac{1}{n} \phi(\{u_{ij}(\{r_{ij}\}), a_{ijk}\}) \] (131)

where \( \omega_{n} \) was defined in (35), masses \( m_{ij} \) are the staging masses from (120), with index \( i \) pointing the particles.

The next target is the prefactor of the Fourier quadratic term. Consider a variable transform:

\[ \tilde{a}_{ijk} \equiv \frac{k\pi}{\sqrt{2}} a_{ijk} \] (132)

Then, the BF trajectory representation (40) changes as:

\[ r_{ij}(\xi) = r_{ij} + (r_{ij+1} - r_{ij}) \xi + \sum_{k=1}^{k_{\text{max}}} \frac{\sqrt{2}}{k\pi} \tilde{a}_{ijk} \sin(k\pi \xi) \] (133)

In the matter of fact, nothing except re-denotation has been done. Gathering all together, for the partition function we get:

\[ Z(\beta) \approx \int \exp \left[ -\beta U^{BF}(\{u_{ij}, a_{ijk}\}) \right] \cdot \prod_{i=1}^{N} \prod_{j=1}^{n} \left( du_{ij} \prod_{k=1}^{k_{\text{max}}} d\tilde{a}_{ijk} \right) \] (134)

We used proportionality sign instead of equality, since the normalizing term was omitted. The Hamiltonian \( H^{BF} \) is defined in (130), with \( U_{\text{eff}}^{BF} \):

\[ U_{\text{eff}}^{BF}(\{u_{ij}, a_{ijk}\}) = \sum_{i=1}^{N} \sum_{j=1}^{n} \frac{\omega_{n}^2}{2} \left( m_{ij} u_{ij}^2 + m \sum_{k=1}^{k_{\text{max}}} \tilde{a}_{ijk}^2 \right) + \frac{1}{n} \phi(\{u_{ij}(\{r_{ij}\}), a_{ijk}\}) \] (135)

The system moves in the phase space, according to the Hamiltonian equations of motion (64), with the generalized coordinates\(^{10}\) \( u_{ij}, a_{ijk} \) and conjugated momenta \( p_{ij}, p_{ijk} \). Note, that masses \( \tilde{m}_{ij} \) and \( \tilde{m}_{ijk} \) should not necessarily coincide with \( m_{ij} \) and \( m_{ijk} \). We set \( \tilde{m}_{ijk} = \tilde{m}_{ij} \), the latter defined the same way as in (122). I would like to underline, that BF-PIMD derived from Eqs. (134) and (135) is not the same as the one derived from Eqs. (41) and (42), though it yields the same result.

\(^{10}\)From here and further tildes upon Fourier amplitudes are omitted
Now, let us consider the case of identical particles. In Sec. 3.4 the formalism for the pure bead case was presented. Previously, PIMD approach for identical particles was considered by Miura and Okazaki [83]. Their PIMD was based on the (anti)symmetric propagator approach of Takahashi and Imada [46] (see Eqs. (46) and (47) in Sec. 3.4). The partition function for fermionic systems reads:

$$Z = \frac{1}{(N!)^n} \int \left( \prod_{i=1}^{N} \prod_{j=1}^{n} \text{d} \mathbf{r}_j^{(i)} \right) \cdot \prod_{j=1}^{n} \det A_j \times \exp \left[ -\frac{\beta}{n} \phi(\{\mathbf{r}_j^{(i)}\}) \right]$$

(136)

where matrix $A_j$ is $N \times N$ matrix, whose matrix elements are defined as:

$$A_j^{(i)} = \left( \frac{mn}{2\pi \hbar^2} \right)^{d/2} \exp \left[ -\frac{\beta m \omega^2}{2} (\mathbf{r}_j^{(i)} - \mathbf{r}_{j+1}^{(i)})^2 \right]$$

(137)

Since the determinant can be negative, the following trick [16, 46] is used. Consider an observable, represented by the operator $\hat{O}$ with the corresponding estimator $\epsilon_O(\{\mathbf{r}_j^{(i)}\})$. Then the canonical average of the observable $\hat{O}$:

$$\langle \hat{O} \rangle = \frac{\int \left( \prod_{i=1}^{N} \prod_{j=1}^{n} \text{d} \mathbf{r}_j^{(i)} \right) \prod_{j=1}^{n} \det A_j \cdot \epsilon_O(\{\mathbf{r}_j^{(i)}\}) \exp \left[ -\frac{\beta}{n} \phi(\{\mathbf{r}_j^{(i)}\}) \right]}{\int \left( \prod_{i=1}^{N} \prod_{j=1}^{n} \text{d} \mathbf{r}_j^{(i)} \right) \prod_{j=1}^{n} \det A_j \exp \left[ -\frac{\beta}{n} \phi(\{\mathbf{r}_j^{(i)}\}) \right]}$$

$$= \frac{\int \left( \prod_{i=1}^{N} \prod_{j=1}^{n} \text{d} \mathbf{r}_j^{(i)} \right) \prod_{j=1}^{n} |\det A_j| \cdot \epsilon_O(\{\mathbf{r}_j^{(i)}\}) \exp \left[ -\frac{\beta}{n} \phi(\{\mathbf{r}_j^{(i)}\}) \right] \cdot \text{sgn}(\det A_j)}{\int \left( \prod_{i=1}^{N} \prod_{j=1}^{n} \text{d} \mathbf{r}_j^{(i)} \right) \prod_{j=1}^{n} |\det A_j| \cdot \epsilon_O(\{\mathbf{r}_j^{(i)}\}) \exp \left[ -\frac{\beta}{n} \phi(\{\mathbf{r}_j^{(i)}\}) \right] \cdot \text{sgn}(\det A_j)}$$

(138)

where $\langle \ldots \rangle_{\|}$ means the averaging with respect to artificial probability distribution $\prod_{j=1}^{n} |\det A_j| \exp \left[ -\frac{\beta}{n} \phi(\{\mathbf{r}_j^{(i)}\}) \right]$, $\text{sgn}$ being the sign function. In other words, we perform a simulation according to always positive artificial probability distribution (being the modulus of the original distribution) and recover true thermodynamic averages from this “unphysical” MD trajectory. Note,

11Estimators were considered in Sec. 3.5
that the origin of the sign problem is clearly pointed out in Eq. (138). When
the exchange effect is strong, all permutations have approximately the same
probabilities, tending the average sign to zero. Thus, we have a very small
number in the denominator, resulting in a dramatic uncertainty growth.

In an attempt to write down the partition function in a more convenient
form, the effective potential \( W_{\text{eff}} \) is introduced, defined as:

\[
W_{\text{eff}} \equiv \frac{1}{n} \phi(\{r_j^{(i)}\}) - \frac{1}{\beta} \sum_{j=1}^{n} \ln |\det A_j| \quad (139)
\]

resulting in the following expression for the partition function:

\[
Z \approx \int \prod_{i=1}^{N} \prod_{j=1}^{n} \text{d}r_j^{(i)} \exp \left[ -\beta W_{\text{eff}}(\{r_j^{(i)}\}) \right] \quad (140)
\]

Thus, \( W_{\text{eff}} \) is the effective potential indeed. Note a very important property
of the effective potential (139):

\[
|\det A_j| \to 0 \Rightarrow W_{\text{eff}} \to +\infty \quad (141)
\]

It means, that there exists an infinite energy barrier, at “nodal surfaces”
defined as \( \det A_j = 0 \). Since molecular dynamics is continuous, it would not be
able to cross the barrier under any circumstances. Thus, molecular dynamics
according to Miura and Okazaki [83] is, in fact, similar to restricted path
integral approach of Ceperley [67], whose applicability is doubtful, since it
gives an incorrect result, e.g., for the ideal Fermi gas [68]. To their excuse, I
should mention, that they have tested their approach for the fermionic case,
only on a system, consisting of three particles in a one-dimensional harmonic
well. The remarkable feature of antisymmetric propagator approach, applied
to one-dimensional systems is, that sign is always positive [128]. Hence, they
were not able to notice the failure of the approach.

To conclude the criticism, I should mention, that their actual formalism
slightly differs from the one presented above. Namely, instead of the effective
potential \( W_{\text{eff}} \) (139) they used the following expression:

\[
W_{\text{eff}} \equiv \sum_{i=1}^{N} \sum_{j=1}^{n} \frac{m \omega_i^2}{2} (r_j^{(i)} - r_{j+1}^{(i)})^2 + \frac{1}{n} \phi(\{r_j^{(i)}\}) - \frac{1}{\beta} \sum_{j=1}^{n} \ln |\det \tilde{A}_j| \quad (142)
\]

where matrix \( \tilde{A}_j \) is also a \( N \times N \) matrix, whose elements are defined by the
relation: \( \tilde{A}_j^{(i)} \equiv A_j^{(i)} / A_j^{(i)} \). Afterwards, they carry out MD with respect
to the normal mode variable transform [127, 78]. The idea is clear: to extract the
Summary and discussion of the papers

identical permutation from the determinant, and to scale terms, corresponding to the other permutations by it. Then, the normal mode transform is supposed to provide the effective dynamics. In fact, the exchange effective potential is considered as a perturbation to the identical permutation, which has sense only if exchange effects are weak. Otherwise, the identical permutation has no benefits over the others. Thus, this approach can be an option when the exchange is weak, but “real” quantum systems, like electrons, in my opinion, require another approach. The possible recipe, overcoming the both problems is suggested below.

Let us start from Eq. (136).12 Again, consider an observable, represented by the operator \( \hat{O} \) with the corresponding estimator \( \epsilon_O(\{r_j^{(i)}\}) \). Then the canonical average of the observable \( \hat{O} \):

\[
\langle \hat{O} \rangle = \frac{\int \left( \prod_{i=1}^{N} \prod_{j=1}^{n} dr_j^{(i)} \right) \prod_{j=1}^{n} \det A_j \times \epsilon_O(\{r_j^{(i)}\}) \exp \left[ -\frac{\beta}{n} \phi(\{r_j^{(i)}\}) \right]}{\int \left( \prod_{i=1}^{N} \prod_{j=1}^{n} dr_j^{(i)} \right) \prod_{j=1}^{n} \det A_j \exp \left[ -\frac{\beta}{n} \phi(\{r_j^{(i)}\}) \right]} \sqrt{(\det A_j)^2 + \delta}
\]

\[
= \frac{\int \left( \prod_{i=1}^{N} \prod_{j=1}^{n} dr_j^{(i)} \right) \prod_{j=1}^{n} \frac{\det A_j}{\sqrt{(\det A_j)^2 + \delta}} \exp \left[ -\frac{\beta}{n} \phi(\{r_j^{(i)}\}) \right]}{\int \left( \prod_{i=1}^{N} \prod_{j=1}^{n} dr_j^{(i)} \right) \prod_{j=1}^{n} \frac{\det A_j}{\sqrt{(\det A_j)^2 + \delta}}} \exp \left[ -\frac{\beta}{n} \phi(\{r_j^{(i)}\}) \right] \sqrt{(\det A_j)^2 + \delta}
\]

\[
= \langle \epsilon_O(\{r_j^{(i)}\}) \frac{\det A_j}{\sqrt{(\det A_j)^2 + \delta}} \rangle \langle \frac{\det A_j}{\sqrt{(\det A_j)^2 + \delta}} \rangle_f
\]

\[
\langle \ldots \rangle_f \text{ means averaging with artificial probability distribution } f:
\]

\[
f \equiv \prod_{j=1}^{n} \sqrt{(\det A_j)^2 + \delta} \exp \left[ -\frac{\beta}{n} \phi(\{r_j^{(i)}\}) \right]
\]

\[
\delta \text{ being any positive number. Note, that } \sqrt{(\det A_j)^2 + \delta} \text{ is not the only function class, that solves the problem. For instance, } (\det A_j)^2 + \delta \text{ would manage, as well. I choose it to be the square root, because:}
\]

\[
\frac{\det A_j}{\sqrt{(\det A_j)^2 + \delta}} \rightarrow \text{sgn}(\det A_j), \quad |\det A_j| \gg \delta
\]

Note, that if we set \( \delta = 0 \) the approach becomes identical to the original one of Miura and Okazaki [83]. So, we perform a simulation according to always

---

12 The derivation does not depend on the scheme used, and, hence, I consider pure bead case, as formulas are less cumbersome.
positive artificial probability distribution $f$ \((144)\) and recover true thermodynamic averages from this unphysical MD trajectory according to \((143)\). Following Miura and Okazaki \cite{83}, we introduce the effective potential $W_{\text{eff}}$:

$$W_{\text{eff}} \equiv \frac{1}{n} \phi(\{r_j^{(i)}\}) - \frac{1}{\beta} \sum_{j=1}^{n} \ln \left(\det A_j\right)^2 + \delta \quad \text{(146)}$$

When $\delta > 0$ the effective potential\(^{13}\) reaches only a finite maximum at nodal surface. Thus, the problem of infinite potential barrier disappears. The height of the finite barrier at nodal surface is determined by the particular value of the parameter $\delta$. The expression for the partition function coincides with Eq. \((140)\).

Now, let us investigate the structure of the determinant $\det A_j$:

$$\begin{vmatrix}
\exp \left[ -\frac{\beta m \omega_n^2}{2} (r_j^{(1)} - r_{j+1}^{(1)})^2 \right] & \ldots & \exp \left[ -\frac{\beta m \omega_n^2}{2} (r_j^{(1)} - r_{j+1}^{(N)})^2 \right] \\
\exp \left[ -\frac{\beta m \omega_n^2}{2} (r_j^{(N)} - r_{j+1}^{(1)})^2 \right] & \ldots & \exp \left[ -\frac{\beta m \omega_n^2}{2} (r_j^{(N)} - r_{j+1}^{(N)})^2 \right]
\end{vmatrix} \quad \text{(147)}$$

I suggest to decompose quadratic expressions under exponents. Matrix elements of $A_j$:

$$A_j^{(i)} = \exp \left[ -\frac{\beta m \omega_n^2}{2} \left( (r_j^{(i)})^2 - 2r_j^{(i)} \cdot r_{j+1}^{(i)} + (r_{j+1}^{(i)})^2 \right) \right] \quad \text{(148)}$$

The exponent in the right hand side of Eq. \((148)\) can be split into product of three exponents. Note now, that all exponents in the first column contain the term: $\exp \left[ -\beta m \omega_n^2 (r_{j+1}^{(i)})^2 / 2 \right]$, while all exponents in the first row contain the term: $\exp \left[ -\beta m \omega_n^2 (r_j^{(i)})^2 / 2 \right]$. The generalization of the latter statement is obvious. Row or column with number $i$ contains the gaussian with $(r_j^{(i)})^2$ or $(r_{j+1}^{(i)})^2$, correspondingly. Thus, using the well known property of the determinants, that multiplication of a determinant by a factor is equivalent to multiplication of any its row/column by the same factor, one gets:

$$\prod_{j=1}^{n} \det A_j = \exp \left[ -\beta m \omega_n^2 \sum_{i=1}^{N} \sum_{j=1}^{n} (r_j^{(i)})^2 \right] \times \prod_{j=1}^{n} \det B_j \quad \text{(149)}$$

where $B_j$ is $N \times N$ matrix, whose matrix elements are:

$$B_j^{(i)} = \exp \left[ -\beta m \omega_n^2 r_j^{(i)} \cdot r_{j+1}^{(i)} \right] \quad \text{(150)}$$

\(^{13}\)Strictly speaking, not the effective potential itself, but its second term in \((146)\).
Finally, the effective potential $W_{\text{eff}}$:

$$ W_{\text{eff}} = m \omega_n^2 \sum_{i=1}^{N} \sum_{j=1}^{n} (r_j^{(i)})^2 + \frac{1}{n} \phi(\{r_j^{(i)}\}) - \frac{1}{\beta} \sum_{j=1}^{n} \ln \sqrt{(\det B_j)^2 + 1} \quad (151) $$

One sees, that the first term is the sum of uncoupled oscillators with twice bigger masses\(^{14}\) than the particles’ mass. Thus, we have obtained the analogue of staging formula, that can provide the similar time scales for all degrees of freedom during the MD run. I want to stress, that here we did not choose any “privileged” permutation.

In conclusion, let us write down the partition function for the BF scheme, obtained by the similar application of ideas, described above:

$$ Z \approx \int \prod_{i=1}^{N} \prod_{j=1}^{n} \left( dr_j^{(i)} \prod_{k=1}^{K} d\tilde{a}_{ijk} \right) \exp \left[ -\beta H^{\text{BF}}(\{r_j^{(i)}, \tilde{a}_{ijk}\}) \right] \quad (152) $$

where the Hamiltonian $H^{\text{BF}}$ reads:

$$ H^{\text{BF}} = \sum_{i=1}^{N} \sum_{j=1}^{n} \left( \frac{p_j^{(i)}}{2m} + \sum_{k=1}^{k_{\text{max}}} \frac{p_{j;k}^{(i)}}{2m_k} \right) + U_{\text{eff}}^{\text{BF}}(\{r_j^{(i)}, a_{ijk}\}) \quad (153) $$

while the $\tilde{m} = 2m$ denotes the new mass, while the effective potential $U_{\text{eff}}^{\text{BF}}$:

$$ U_{\text{eff}}^{\text{BF}}(\{r_j^{(i)}, a_{ijk}\}) = \sum_{i=1}^{N} \sum_{j=1}^{n} \frac{\tilde{m} \omega_n^2}{2} \left( (r_j^{(i)})^2 + \sum_{k=1}^{k_{\text{max}}} a_{ijk}^2 \right) - \frac{1}{\beta} \sum_{j=1}^{n} \ln \sqrt{(\det B_j)^2 + 1} \quad (154) $$

and the matrix elements of $B_j$:

$$ B_j^{(\hat{i})} = \exp \left[ -\beta \tilde{m} \omega_n^2 \frac{r_j^{(\hat{i})}}{2} \cdot \frac{r_j^{(i)}}{n} - \frac{\beta}{n} \int_0^1 d\xi \phi \left( r_j^{(i)}(\xi) \right) \right] \quad (155) $$

where the trajectory representation $r_j^{(\hat{i})}(\xi)$ is as follows:

$$ r_j^{(\hat{i})}(\xi) = r_j^{(i)} + (r_{j+1}^{(i)} - r_j^{(i)}) \xi + \sum_{k=1}^{k_{\text{max}}} \frac{2}{k \pi} a_{ijk} \sin(k \pi \xi) \quad (156) $$

The details of the BFPIIMD carried out according to Eqs. (152)-(156) are given in Paper IV.

\(^{14}\)This can be considered as frequencies being greater by the factor $\sqrt{2}$. I prefer to treat it as the mass increase.
5.2 Harmonic oscillator

Although one might say that there is nothing more simple than harmonic oscillator (HO), it is probably the most complicated small system to simulate by means of MD, from the ergodicity point of view. The problem of non-ergodic behaviour of HO is discussed in details in Sec. 4.3. In Paper II the one-dimensional quantum HO is simulated as a test system for the BFPIMD. HO can be naturally expressed in intrinsic units, namely, inverse temperature, frequency and mass. Interesting and useful property of the quantum HO is, that in intrinsic units, it can be completely identified by only one parameter: $b \equiv \beta \hbar \omega$. Another feature of HO is, that the potential energy integrals, as well as integrals for forces, can be evaluated analytically (see Eqs. (16,17)).

In order to test the correct work of the thermostats, the momenta distributions are compared with the analytical ones (31)-(33). The distributions themselves and the differences between exact and simulation distributions are presented in Fig. 1. As it follows from Fig. 1(b), the distributions tend to analytical ones with the number of beads and Fourier harmonics, while thermostats work fine even for only 2 beads and 1 Fourier amplitude. Hence, the latter, being the “worst” result, is presented in Fig. 1(a). The similar results were obtained for all other systems studied. As an example, see Fig. 6 in Paper II for the same distributions and their differences, which refer to the case of Hydrogen atom.

Two types of the estimators were considered: continuous and pure bead ones. The former were obtained by taking the averaged value with respect to the whole trajectory. Technically, it means, that each time slice contributes by $10 - 20$ equally separated points, which corresponds to the numerical integration of the estimator over the whole trajectory according to the trapezoid rule. The latter uses only the estimator’s values in the vortex points, i.e., on beads.

Somewhat counter-intuitively, we discovered, that use of pure bead estimators within the Bead-Fourier MD scheme provides a better convergence relative to the number of beads (see Tab. 1). There exists, however, a reasonable explanation for that. If one considers the numerical evaluation of the integral of $x^2$ using the trapezoidal rule (analogue of the pure bead estimator), it will always be greater than its exact value (the continuous estimator). Since in the finite-bead approximation of path integrals the potential energy is underestimated, we have a clear case of cancellation of errors. Situation may be different in the case of convex potential functions (with negative second derivative) but these are not typical cases. Important is also that both estimators provide exact values at infinite number of beads.

Note, that the energy dependence on the number of Fourier harmonics shows, that the biggest difference in energies occurs between zero and one

\[\text{In this subsection all references on equations refer to Paper II, unless otherwise pointed.}\]
Figure 1: The comparison of classical momentum distributions for quantum harmonic oscillator with corresponding analytical results. (a) The pairs of simulation results and analytical curves for total, internal and mass centrum momenta. (b) The difference between simulation and analytical total momenta. Momenta are presented in intrinsic units. Figure coincides with Fig. 1 from Paper II.
Table 1: Quantum mean energy for harmonic oscillator at $b = 2$ for various numbers of beads $n$ and Fourier harmonics $k_{\text{max}}$. The first row in each cell corresponds to continuous estimators, while the second - to pure bead ones. Energies are presented in intrinsic units. The exact energy value is: 0.656. Table is the same as Table 1 in Paper II.

<table>
<thead>
<tr>
<th>$k_{\text{max}}$</th>
<th>Number of beads, $n$</th>
<th>2</th>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0</td>
<td>0.530</td>
<td>0.571</td>
<td>0.585</td>
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<tr>
<td></td>
<td></td>
<td>0.607</td>
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<td>0.647</td>
</tr>
<tr>
<td>1</td>
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<td>0.613</td>
<td>0.624</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.650</td>
<td>0.655</td>
<td>0.655</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>0.612</td>
<td>0.632</td>
<td>0.637</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.649</td>
<td>0.659</td>
<td>0.657</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>0.623</td>
<td>0.628</td>
<td>0.642</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.650</td>
<td>0.646</td>
<td>0.656</td>
<td></td>
</tr>
<tr>
<td>4</td>
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<tr>
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</tr>
<tr>
<td></td>
<td>0.648</td>
<td>0.655</td>
<td>0.658</td>
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</table>

Fourier amplitudes used, i.e., between pure bead and Bead-Fourier dynamics. Note also, that the energy values for the same total numbers of degrees of freedom (obtained by different combinations of $n$ and $k_{\text{max}}$) are nearly the same. This can be considered as an illustration of Coalson’s isomorphism [51].

Pure bead and continuous quantum coordinate distributions are compared with the exact results in Fig. 2. Note, that already for the number of beads $n = 2$ and only one single Fourier harmonic, the pure bead coordinate distribution nearly coincides with the exact one, while the deviations of the continuous one are relatively big. This illustrates that the averages calculated over beads only, are better than those calculated over the whole trajectory. I want to stress, that in both cases the dynamics was derived according to the Bead-Fourier scheme, i.e., forces acting on beads depend on the whole trajectory. Again, the pure bead dynamics yields worse results, moreover it suffers from ergodicity problems.

The data presented above, corresponds to a weakly degenerated system. Now, let us consider a strongly degenerated case with $b = 15.8$. The tempera-
Figure 2: The quantum coordinate distribution for harmonic oscillator at $b = 2$. (a) Comparison between the results obtained via “continuous” and “pure bead” estimators and the analytical ones for $n = 2, k_{\text{max}} = 1$. (b) The differences between two quantum coordinate distributions for: $n = 2, k_{\text{max}} = 1; n = 4, k_{\text{max}} = 7$ and the analytically exact distribution. Distances are given in intrinsic units. Figure coincides with Fig. 4 from Paper II.
Figure 3: Quantum harmonic oscillator at $b = 15.8$. The dependences of the quantum mean energy (in intrinsic units) over beads numbers for various numbers of Fourier harmonics. Comparison with the exact result. Figure coincides with Fig. 5 from Paper II.

ture is chosen in order to compare BFPIMD with the staging pure bead scheme of Tuckerman [72]. HO at such reduced temperature $b = \beta\hbar\omega$ roughly corresponds to $OH$–bond vibrations in water at room temperature. The results for the quantum mean energy for a different number of beads and Fourier components are presented in Fig. 3. For instance, for the number of beads $n = 5$ any number of Fourier harmonics $k_{max} \geq 2$ gives results inside the statistical error. Within the pure bead algorithm, it would be necessary to take several hundred beads to reach the same precision. In work [72] $n = 400$ was used to simulate a HO at this temperature, yielding about the same accuracy (0.3%). One might argue, that for any case of interest one would have to integrate all integrals numerically (which is not the case in the pure bead scheme), resulting in the increase of space points involved, and, hence, the raise of computational expenses at least by an order of magnitude. My objection is, that the main profit is gained by the decrease of the chain frequency (which is proportional to the square root of beads’ number) resulting in the proportional increase of the MD time step. Thus, if we consider number of beads $n = 4$ instead of 400, then we can increase time step 10 times.

Another interesting feature is, that although the number of beads and
Summary and discussion of the papers

Fourier harmonics have to be increased as \( h \) is growing, the increased CPU time is somewhat compensated by the possibility to increase the size of the MD time step, since the stiffness of the springs is proportional to \( n/h^2 \). Thus, the statement: “Making the temperature lower results in the increase of the computational time” is at least doubtful. Moreover, as the number of beads involved in BF scheme is much less than those in pure bead scheme, their increase does not lead to severe ergodicity problems.

5.3 Harmonic Helium atom

Before applying the developed methodology to real atoms and molecules, I present first a “harmonic helium atom”, in which two interacting electrons move in a harmonic field. The reason of considering this model is that it is probably the only case of two-electron system in external field having an analytical solution [129]. Solutions are available for a discrete set of frequencies. Here we consider the ground state \((l = 0)\) and \( n = 2, 3 \) resulting in frequencies \( \omega_r = 0.25, 0.05 \) correspondingly. We present data for the pair correlation function \( G(r) \) and the charge density \( n(r) \). The former can be obtained from the formula for \( G(r) \) in work [129] by the integration over angles in spherical coordinates system resulting in:

\[
G(r) = \exp \left[ -\omega_r r^2 \right] t_n^2(r) \tag{157}
\]

where \( t_n(r) \) is the polynomial of order \( n \), namely:

\[
t_2(r) = r a_0 \left( 1 + 0.5 \cdot r \right), \quad t_3(r) = r a_0 \left( 1 + 0.5 \cdot r + \omega_r r^2 \right) \tag{158}
\]

where \( a_0 \neq 0 \).

The charge density \( n(r) \) is a 3-dimensional convolution integral between the internal and center-of-mass motions:

\[
n(r) = \int dr' G(r') \cdot \xi^2 \left( r + \frac{r'}{2} \right) \tag{159}
\]

where \( \xi(r) = \exp \left[ -0.5 \omega_R r^2 \right] \) - is the ground-state wave-function of the harmonic oscillator with frequency \( \omega_R = 4 \omega_r \).

Both functions \( G(r) \) and \( n(r) \) are presented in Fig. 4 with the distances scaled by the “classical electron distance” \( r_0 = (2 \omega_r)^{-\frac{1}{2}} \). Both functions are normalized to unity. One can see, that the coincidence of simulation results with the analytical solutions is perfect both for the charge density and for the pair electron correlation. The small deviations near zero distance in the simulation curves of the charge density are related to the insufficient statistics (finiteness of the MD run).

\[16\] All denotations in this subsection coincides with original ones, introduced by Taut [129]
5.4 Hydrogen atom and Helium ion

Another realistic and analytically solvable quantum system is the Hydrogen atom (HA), presented as a single electron (trajectory) in an external Coulomb field of the nucleus (proton). In order to avoid an infinite negative potential energy at zero distance, we change the Coulombic potential to a parabolic one, at distances less than some cutoff radius $r_0$. The parameters of the potential inside the cut-off are fixed by the conditions that the potential and its first derivative must be continuous [64], resulting in:

$$V(r) = \begin{cases} 
-\frac{Z^2}{4\pi\varepsilon_0 r_0} \left( \frac{r}{r_0} - \frac{3}{2} \right) & r \geq r_0 \\
-\frac{Z^2}{4\pi\varepsilon_0 r_0} \left( \frac{r^2}{2r_0^2} - \frac{3}{2} \right) & r \leq r_0
\end{cases} \quad (160)$$

Now we have to integrate the potential terms numerically. It seems important to point out, that in the case of smoothed potential (160), we have to check, for each trajectory point, is it inside or outside the cutoff radius. Thus, the
Table 2: Quantum mean energy (eV) for hydrogen atom presented for various numbers of beads \( n \) and Fourier harmonics \( k_{\text{max}} \). The first row in each cell corresponds to “continuous” estimators, while the second - to “pure bead” estimators. The table coincides with Table 3 in Paper II.

<table>
<thead>
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<th>( k_{\text{max}} )</th>
<th>Number of beads, ( n )</th>
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<td>-20.5</td>
</tr>
</tbody>
</table>

Possibility to perform integrations analytically is useless, even if we would manage to do it.

Basically, we are forced to use cutoff in order to carry out the correct dynamics, i.e., to limit forces below some maximum value. And we should emphasize that it is not possible to decrease the cutoff radius infinitely and even significantly, because we have to increase the beads’ number proportionally in order to compensate the increase of potential stiffness.

The results for the comparison of classical momenta distributions and their deviations from the exact ones are not shown. I just want to mention, that those deviations are of the similar type as for HO (Fig. 1(b)), but are one order of magnitude smaller. The reason is that simulations of the Coulomb potential require more beads than the harmonic oscillator, while the deviations of momenta from the Maxwell distribution decrease with the number of beads.

Quantum mean energy dependence on the number of beads and Fourier amplitudes for HA is presented in Tab. 2. Note, that as it was in the case of the quantum harmonic oscillator, the average energies obtained by pure bead estimators converge faster than those obtained by using Bead-Fourier estimators. One can also see a very clear improvement of the results after addition of the Fourier harmonics. It is especially well seen from the quantum
Figure 5: The quantum coordinate distributions for hydrogen atom with $n = 30$ and various numbers of Fourier harmonics. Comparison with the analytical result. Distances are given in Å. Figure coincides with Fig. 8 from Paper II.

coordinate distributions, shown in Fig. 5. It is clear, that the distributions for the pure bead case and for BF with only one harmonic, differ not only quantitatively, but qualitatively. In other words, without Fourier harmonics the trajectory becomes easily stacked to the nucleus.

In the matter of fact, softening the potential according to (160) leads to problems, as immediately arouse when we started to simulate Helium ion. Mathematically, the difference between HA and Helium ion is only in the doubled charge, and the fact, that the maximum of the radial distribution function (RDF) is twice closer to the nucleus.

Let us investigate the consequences of the potential softening (160). The potential energy can be obtained (besides the averaging of the proper estimator) by integration of the interaction potential with the electron density. If we consider, e.g., a HA and integrate numerically the potential (160) together with the analytically calculated electron density, we get the exact potential energy value for our smoothed potential. Our analysis shows that if we take the cut-off $r_0 = 0.1\,\text{Å}$ (which was the typical value both in Paper II and Paper III) then the $E_{\text{pot, smooth}} = -26.9\text{eV}$, while the exact one for HA is $-27.2\text{eV}$. The influence
of the cutoff on the potential energies is obvious and significant. Of course, the kinetic energy also changes and, in the case of HA, an almost perfect cancellation of errors takes place. But the fact, that the cancellation of errors happens for HA does not mean that it will necessarily occur for any other system.

A possible solution could be to derive dynamics from the potential (160) and to integrate the density obtained with the unsmoothed potential. This idea would work under assumption, that the electronic density is only slightly perturbed by the potential softening. If one looks in Fig. (6)(a) the answer seems obvious: density is not perturbed, as eye can hardly see the deviations of the simulation distributions from the exact ones. Unfortunately, the latter is incorrect. In order to relate the deviations in the RDFs with the induced errors on the potential energy we define a function $f(r)$:

$$f(r) \equiv \frac{e^2 [\rho_{ex}(r) - \rho(r)]}{4\pi\epsilon_0 r}$$

which is related to the potential energy error as:

$$\frac{\Delta E_{H,He^+}}{Z_{H,He^+}} = \int_0^\infty f(r) \, dr$$

where $Z_{H,He^+}$ is the atomic number of the corresponding atom, $\rho(r)$ and $\rho_{ex}(r)$ are the simulated and exact RDFs, respectively. Function $f(r)$ shows how RDF deviation at any given distance affects the final energy result (see Fig. 6(b)). While the deviations for HA are rather small, those for the Helium ion are huge and can cause errors in energies up to several eV. The conclusion is: softening the Coulomb potential introduces an artifact in the electronic density distribution and causes serious errors in the energies if the nucleus charge is greater than one. That is why direct application of the smoothed potential (160) is not an optimal choice. The problem is, thus, clear: to construct an effective Coulomb potential without singularity, resulting in the correct electronic density. The possible recipe, suggested in Paper III is as follows:

First, consider hydrogenic atoms. On the one hand, the analytical solution of the Schrödinger equation is known and, hence, the exact radial distribution function for the ground state [130]:

$$\rho_{ex}(r) = \frac{4Z^3 r^2}{a_0^3} \exp \left[ -\frac{2Zr}{a_0} \right]$$

On the other hand we can compute the RDF induced by our smoothed potential. So, we can define the correction potential using the well known technique:

$$V^{corr}(r) = \frac{1}{\beta} \ln \left[ \frac{\rho_{ex}(r)}{\rho(r)} \right]$$
Figure 6: (a) Exact (solid lines) and simulation RDFs for Hydrogen atom (asterisks) and Helium ion (circles). (b) Function $f(r)$ defined in (161) for Hydrogen atom and Helium ion.
where $V^{corr}(r)$ is the correction to the smoothed potential (160). Note, that the correction is applied only for beads. More precisely, the correction affects only forces acting on beads. The force correction may be determined by differentiation of Eq. (164):

$$\frac{\partial V^{corr}(r)}{\partial r} = -\frac{1}{\beta} \left[ \frac{\rho'_x(r)}{\rho_x(r)} - \frac{\rho'(r)}{\rho(r)} \right]$$  \hspace{1cm} (165)

resulting in:

$$f^{corr}(r_{ij}) = -\frac{\partial V^{corr}(r_{ij})}{\partial r_{ij}} \sum_{l=1}^{L} \frac{x_{ijl}}{x_{ijl}}$$  \hspace{1cm} (166)

where $f^{corr}(r_{ij})$ is the force correction wanted. Strictly speaking, the iterative procedure should be carried out: obtain the correction potential according to (165), run the MD-program using corrected forces (166) and obtain the next order correction. Repeat this procedure until the convergence is reached.

The scheme described above works straightforwardly for hydrogenic atoms (as we know the analytical solution for the density). Since the correction potential is significant only in the small region close to nuclei, one can hope that it would be possible to use the same potential designed for hydrogenic atoms for studying of many-electron systems with interaction and exchange. Indeed, the probability of two electrons to be found on the nucleus simultaneously is very small and, hence, we can assume that interaction would not influence the structure of the electronic density around the nucleus dramatically.

One can note some analogy between the correction potentials introduced in the present work and pseudopotentials used in many quantum-chemical methods, for example in the density functional theory. In quantum chemistry, pseudopotentials are used not only to mimic internal electrons in atoms (if only external electrons are considered), but they are also introduced for atoms without internal electrons like Hydrogen. In the last case the pseudopotentials, by smoothing the core region, allow to use smaller basis sets, in a similar manner as correction potentials in the PI approach make it possible to use less number of beads or Fourier components. The specific form of pseudopotentials or correction potentials is, however, different for different methods, since it depends on the specific relationships between the potential and the electron density within each method and the approximations used.

5.5 **Hydrogen molecule and molecular ion**

Let us first consider data for the hydrogen molecule ion. In Fig. 7 we present the ground state energies of a hydrogen molecule ion for different nuclei-nuclei distances. The “exact” curve was obtained by the full Configuration
Interaction computations. The energies are calculated both using corrected and non-corrected potentials via pure bead estimators. One can see that there exists a systematic shift between the energies obtained using estimators with different cutoff radii and the ones with the smaller radius are obviously better. The latter confirms that the cancellation of errors, induced by the smoothed potential for hydrogen molecule ion is incomplete. The accuracy of the energies presented was around $\frac{1}{2}eM$ which means that both corrected and non-corrected potentials provide satisfactory results. The picture for hydrogen molecule is qualitatively the same (see Fig. 8 in Paper III).

One can try to extract vibrational frequencies from the data obtained. Let us approximate the effective nuclei-nuclei interaction by parabola with cubic unharmonicity. The vibrational frequency for the hydrogen molecule obtained by the least square fitting is $4292cm^{-1}$, while the experimental one is $4420cm^{-1}$. For the hydrogen molecule ion the obtained frequency is $2436cm^{-1}$ with the experimental one equal to $2410cm^{-1}$. In fact, the coincidence is almost perfect. The experimental equilibrium distances are equal 0.74Å and 1.06Å for the hydrogen molecule and molecular ion, respectively [130]. Averages obtained by the BFPIMD simulations demonstrate the minima in just
Table 3: The number of “jumps” and “closeness” of the trajectory to the nuclei with respect to inter-nuclei distance are presented.

<table>
<thead>
<tr>
<th>$R_{\alpha\beta}(\text{Å})$</th>
<th>Closeness</th>
<th>Jumps</th>
</tr>
</thead>
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It seems instructive to investigate the behaviour of the hydrogen molecule ion on large inter-nuclei distances. We are interested in the dissociation of the molecule into hydrogen atom and separated nucleus. The behaviour of the total energy, kinetic and potential energies, as well as the interaction energy of the electron with the farther nucleus. All of them must tend to the corresponding energies of the hydrogen atom with inter-nuclei distance. We plotted the differences between the energies of hydrogen molecule ion and their exact limits in Fig. 8. One can see that all differences tend to zero as they should.

For the hydrogen molecular ion, we have also studied the number of trajectory “jumps” between the nuclei and “closeness” of the trajectory to the nuclei. The jump was determined according to the center-of-mass of the trajectory: when it crosses the plane drawn on the equal distance from the nuclei, the trajectory is considered as “jumped”. The closeness was determined as the ratio between the number of beads belonging to the same half-space as the center-of-mass, and the total number of beads. This property measures how confined the trajectory is to the nucleus. The data are presented in Table 3. One can see that jumps become almost impossible when the inter-nuclei distance becomes larger than 4.5Å. Obviously, in such a case the closeness tends to 100%.
Noninteracting particles in external field

As it was already mentioned, the grand canonical approach yields sometimes more simple expressions, than the canonical case. Feynman [2] presented grand canonical thermodynamic potential \( \Omega \) in the form of a series over powers of activity for a system of free spinless bosons in a box. Coefficients of this series include canonical partition functions for cyclic permutations (cycles), hence the whole expression is often called “a series over cycles”. In Paper I a Feynman-type series over cycles is constructed in a more general case, i.e., for a system of noninteracting identical particles (bosons and fermions) with spin in an arbitrary external potential field. Below, I would like to highlight the key points of its derivation.

Consider \( N \) noninteracting identical particles with spin \( s \) at inverse temperature \( \beta \). Assume that the Hamiltonian does not depend on spin (in fact, it means the absence of a magnetic field). We start from the Eq. (45) generalized
Summary and discussion of the papers

for the case of spin particles (see Eqs. (1)-(4) in Paper I). Since, the Hamiltonian
does not depend on spin, the partition function can be split into coordinate
and spin parts, the latter yielding a factor, dependent only on the specific per-
mutation considered. According to the group theory, the permutation group
splits into classes, each of the latter having a specific cycle structure (a set of
indices $C_\nu$). As a result, the canonical partition has the form:

$$Z^{A,S}(\beta) = \sum_{\{C_\nu\}} \prod_{\nu=1}^{N} \frac{a_\nu^{C_\nu}}{C_\nu!}$$

(167)

where $a_\nu$ is defined as:

$$a_\nu \equiv \xi^{\nu-1}(2s+1)Z_\nu(\beta)$$

(168)

In the equations above, $\xi = \pm 1$ for bosons and fermions, respectively, $Z_\nu(\beta)$
is the partition function of a cycle of length $\nu$. Summation over $\{C_\nu\}$ assumes
the condition:

$$\sum_{\nu=1}^{n} \nu C_\nu(P) = N$$

(169)

is fulfilled for each permutation $P$. The latter constraint is very inconvenient,
hence, the grand canonical approach is considered. The starting point is the
general expression for the grand canonical partition function, which has the
form of a series over activity $\lambda = \exp[\beta \mu]$, $\mu$ being the chemical potential (see
Eq. (15) in Paper I). The result for the grand canonical potential is as follows:

$$\beta \Omega^{[A,S]}(\beta, \mu) = -(2s+1) \sum_{\nu=1}^{\infty} \frac{\xi^{\nu-1}}{\nu} Z_\nu(\beta) \lambda^\nu$$

(170)

Note, that obtained series over powers of activity (170) is valid for noninteract-
ing identical particles in an arbitrary external field.

The partition functions $Z_\nu$ have a very important property:

$$Z_\nu(\beta) = Z_1(\nu \beta)$$

(171)

It means that a canonical partition function for a cycle of $\nu$ particles is equal
to that of a single particle at the inverse temperature $\nu \beta$. In other words, $N$-
particle problem can be reduced to that of a single particle in the same field,
but at a set of divisible inverse temperatures.

Note, that Eq. (170) can be obtained from another origin, namely, from the
series over single-particle energy states (see Eqs. (23)-(25) in Paper I). Eq. (25)
in Paper I is obviously equal to Eq. (170) via the property described above
(171).
The other thermodynamic quantities, like number of particles $N$, energy $E$, etc., can be obtained from the grand canonical potential $\Omega$ using its generating properties. Hence, all thermodynamic quantities are explicit functions of chemical potential $\mu$ and inverse temperature $\beta$ and can be obtained both as a series over cycles and series over single-particle energy states (see Eqs. (26), (28), (31), (32) in Paper I). In order to obtain the canonical averages, i.e., those corresponding to the constant number of particles $N$, the following trick is performed. The expressions for number of particles $N(\beta, \mu)$ are treated as equations for obtaining $\mu(\beta)$ dependences at constant $N$. Then, for instance, energy temperature dependence, can be obtained as $E(\beta, \mu(\beta))$. Analogously, the dependences on the chemical potential can be obtained, as well as $\beta$ and $\mu$ dependences of all canonical quantities.

Note, that the series over cycles converge slowly at low temperatures (high $\beta$), and absolutely diverge at $\mu > 0$ (in the fermionic case). But, fortunately, series over single-particle energy states have sense of a low temperature expansion, resulting in the opposite convergence behaviour. Thus, we can obtain all quantities in the region $\mu \leq 0$ for fermions and without restrictions for bosons by both series, which provides an excellent test for the data obtained. Moreover, we compared the energy temperature dependences for fermions with spin $s = 1/2$ in oscillator field for the smallest number of particles ($N = 2, 3$). They can be compared with analytical results obtained in [64]. The relative differences of numerical and exact results are presented in Fig. 3 in Paper I. Note, that maximum deviation does not exceed 7% for $N = 2$ and 3% for $N = 3$. Obviously, for $N \approx 10$ we can completely neglect the difference between the results of averaging in both ensembles. Thus, we can conclude, that numerical calculations of averages at fixed $N$ with the aid of the grand canonical ensemble indeed reproduce the canonical averages.

Two potentials were considered in Paper I: three-dimensional isotropic harmonic field and Pöschl-Teller potential [131]. The latter is defined as:

$$V(x) = \frac{\hbar^2 \alpha^2}{2m} \left[ \frac{\kappa(\kappa - 1)}{\sin^2 \alpha} + \frac{\lambda(\lambda - 1)}{\cos^2 \alpha} \right]$$

(172)

with parameters $\kappa > 1$, $\lambda > 1$ and the range of $x$: $0 \leq x \leq \pi/2\alpha$. It has a smooth bottom and approaches asymptotically vertical walls at limiting values of $x$. The Schrödinger problem for this potential has an exact solution, resulting on the spectrum:

$$E_n = \frac{\hbar^2 \alpha^2}{2m} (\kappa + \lambda + 2n)^2, \ n = 0, 1, 2 \ldots$$

(173)

In conclusion, I want to mention, that this approach was generalized also for systems with magnetic field [132].
6 Conclusion

Two goals were pursued in this thesis. The first goal was to obtain exact expressions for systems of noninteracting identical particles in an arbitrary external field. They were obtained in Paper I in a form of Feynman-type series over cycles, as well as series over single-particle energy states, for the grand canonical partition function and other thermodynamic quantities. A numerical procedure for calculation of the equilibrium properties at constant particles’ number was developed. It was shown, that those properties can be treated as the averages in the canonical ensemble, if the number of particles exceeds a dozen. The important property of noninteracting particles, that the $N$-particle problem can be always reduced to that of a single particle in the same field, but at a set of divisible temperatures, was proved. The technique developed, provides a way to test the simulation methods by applying them to noninteracting particles in the external field.

The second goal was to develop a stable and reliable method for truly ab-initio simulations of quantum systems. Bead-Fourier path integral molecular dynamics was suggested as a possible candidate. In Paper II it was presented in the case of distinguishable particles and applied for quantum harmonic oscillator and the Hydrogen atom. It was demonstrated that Bead-Fourier path integral molecular dynamics accurately reproduces the properties for which the analytical solutions exist. The main attention was paid for the ergodicity problems. It was shown, that Bead-Fourier scheme is preferable to the pure bead one.

The application of the Bead-Fourier path integral molecular dynamics for simulations of the ground states of simple molecules was presented in Paper III. The Hydrogen molecule and molecular ion were considered as examples. It was shown, that the method allows one to reach the accuracy needed for the description of chemical bonds in molecules. It was demonstrated, that softening the Coulomb potential lead to artificial trends in the electron density, resulting in the noticeable errors in the ground state energies for nuclei with atomic numbers greater than one. The correction potential was invented in order to overcome the latter problem.

Paper IV is dedicated to identical particles and questions of dynamics’ efficacy. Staging-type [72] variant of the method was suggested and tested for the case of distinguishable particles. The formalism including quantum statistics was presented. The impossibility of the sign change in the previously known approach [83] was pointed out and the solution was suggested. It was shown, that the formalism developed can be naturally transformed to the form, providing efficient molecular dynamics.

The recent progress gives hope, that Bead-Fourier path integral molecular dynamics is a promising option for quantum simulations.
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The times of my studentship are coming to their logical end and it seems to be a proper moment to look back and thank everyone who helped me and without whose support this thesis would never be accomplished.

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References


