Introduction to Path Integral Monte Carlo. Part I.

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Outline

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1. Introduction
   - Numerical methods for quantum many-body problems
2. Variational Monte Carlo
   - Variational Monte Carlo (VMC)
3. Path-integral Monte-Carlo
   - Quantum mechanical averages and density matrix
   - Path-integrals
4. Conclusion
   - Conclusion

Methods for many-body problems

Many-body Schrödinger equation for Coulomb interaction

$$\hat{H}\Psi(R) = E\Psi(R), \quad \hat{H} = -\frac{\hbar^2}{2m}\sum_i \nabla_i^2 + \sum_i V_{\text{ext}}(\mathbf{r}_i) + \sum_{i<j} \frac{q_i q_j}{|\mathbf{r}_i - \mathbf{r}_j|}$$

We are interested in

- Energy spectrum: ground state, low-excited states.
- Expectation values of operators $\langle \Psi_n | \hat{A} | \Psi_n \rangle \,/\, \langle \Psi_n | \Psi_n \rangle$

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Theoretical approaches (scaling with system size):

1. *Direct diagonalization (CI)* $\sim N^6$*:* – most exact method but only small systems
2. *Mean field (DFT, HF)* $\sim N^3$*:* – large system sizes, approximation on exchange/correlation
3. *Quantum MC (VMC, DMC, GFMC, PIMC)* $\sim N^4$*:* – calculations with full inclusion of many-body correlation effects, most accurate benchmark for medium-large systems

Outline

Variational Monte Carlo (VMC)

Variational Monte Carlo solves the Schrödinger equation stochastically.

- Make an *ansatz* for the wave-function Ψ with some free parameters.
- Attempt to find the optimal parameter set which minimizes the energy.

Consider expectation values of the Hamiltonian on Ψ

$$E_v = \frac{\langle \Psi | \hat{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle} = \int dR \left(\frac{\hat{H}\Psi(R)}{\Psi(R)} \right) \frac{|\Psi(R)|^2}{\int dR' \, |\Psi(R')|^2}$$

$$= \int dR \, E_L(R) \, \rho(R) = \langle E_L(R) \rangle_\rho \, ,$$

where $R = (\mathbf{r}_1, \ldots, \mathbf{r}_N)$, $E_L(R)$ is local energy and $\rho(R) = A \, |\Psi(R)|^2$ is the distribution function.

Main steps of VMC

Goal is to find the best estimation Ψ of a true ground state wave function Ψ_0 by using the *zero-variance principle*, i.e.

$$E_v = \langle E_L(R) \rangle_\rho = \frac{1}{M} \sum_{i=1}^{M} E_L(R_i) \pm \sigma_E / \sqrt{M}$$

$$\sigma_E^2 = \langle (E_L(R) - E_v)^2 \rangle_\rho \xrightarrow{E \to E_0} 0.$$

This is equivalent to the search for the global energy minimum $E[\Psi_0] = \min_\Psi \{ \langle E[\Psi] \rangle \}$.

Algorithm

1. Fix variational parameter set $\{ \lambda \}$
2. Sample R using $\rho(R)$ with a random walk in the space of degrees of freedom
3. Compute average local energy $\langle E_L(R) \rangle_\rho$.
4. Accept parameter as new best estimate if energy is lower than previous best.
5. Change parameter set and go back to step (1).

Variational Monte Carlo (continued)

Jastrow-Slater wave function:

$$\Psi(\mathbf{r}_1, \ldots, \mathbf{r}_N) = J(\mathbf{r}_1, \ldots, \mathbf{r}_N) \sum_k d_k D_k^{\uparrow}(\mathbf{r}_1, \ldots, \mathbf{r}_{N\uparrow})\, D_k^{\downarrow}(\mathbf{r}_{N\uparrow+1}, \ldots, \mathbf{r}_N)$$

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Jastrow factor (Boys and Handy's form)

$$J(\mathbf{r}_1, \ldots, \mathbf{r}_N) = \underbrace{\prod_{\alpha_i} e^{A(r_{i\alpha})}}_{\text{electron-nucleus}} \underbrace{\prod_{i<j} e^{B(r_{ij})}}_{\text{electron-electron}} \underbrace{\prod_{\alpha, i<j} e^{C(r_{i\alpha}, r_{j\alpha}, r_{ij})}}_{\text{electron-electron-nucleus}}$$

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A, B, C are polynomials of scaled variables $\bar{r} = b\,r/(1+\alpha r)$ of the n-order and recover most of the correlation energy $E_{corr} = E_{exact} - E_{HF}$.

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Practical notes:

- Jastrow factors are optimized by variance/energy minimization
- Orbitals and set of d_k coefficients in determinantal part are obtained:
  – Hartree-Fock or DFT (LDA, GGA)
  – CI or multi-configuration self-consistent field calculations
  – Optimized by energy minimization

References: Foulkes et al., Rev.Mod.Phys. 73, 33 (2001);
Filippi, Umrigar, J.Chem.Phys. 105, 213 (1996) and references therein.

Advantages of VMC

- Freedom in choice of trial wave function Ψ
- MC integration allows: a) large system sizes, b) complex forms of Ψ

- Ψ has more compact presentation than Ψ_{CI} in quantum chemistry
- Jastrow and determinants determine two types of correlations:
    - Dynamical correlations: due to inter-electron repulsion (taken by Jastrow factor)
    - Static correlations: due to near-degeneracy of occupied and unoccupied orbitals (taken by linear combination of determinants)
- Determinantal part yields the nodes (zeros) of wave function
    - Determines the fixed-node quality of Diffusion MC, PIMC, etc.

Why go beyond VMC

- Dependence of the results on a trial wave function.
- No systematic procedure to construct analytical form of Ψ. One choses Ψ based on physical intuition.
- Easier to construct good Ψ for *closed* than for *open* shells.
- The VMC wave function optimized for the energy is not necessary well suited for other quantities.

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Quantum mechanical averages for distinguishable particles

- Quantum mechanical average using N-particle wave functions (pure ensemble)

$$\langle A\rangle\,(N,\beta)=\frac{1}{Z}\int dR\;\langle R|\hat{A}|R'\rangle\;\psi^*(R)\,\psi(R)$$

Direct generalization to coherent superposition of N-particle wave functions.

- Finite temperatures ($T>0$, mixed ensemble): use N-particle density matrix $\rho(R,R',\beta)$, which in coordinate representation is a superposition of wavefunctions weighted with probability density, i. e.

$$\rho(R,R';\beta)=\sum_\alpha \psi_\alpha(R)\,\psi_\alpha^*(R')\,e^{-\beta E_\alpha}=\langle R|e^{-\beta\hat{H}}|R'\rangle\equiv\langle R|\hat{\rho}|R'\rangle$$

with N-particle energy eigenvalues E_α and the density operator $\hat{\rho}$. A thermodynamic average can then be computed as

$$\langle A\rangle\,(N,\beta)=\frac{1}{Z}\int dR\;\langle R|\hat{A}|R'\rangle\;\rho(R,R',\beta),$$

Partition function

The partition function is the sum over all accessible states weighted with their thermal probability, i.e

$$Z(N,\beta) = \int dR\, \rho(R,R',\beta) = \mathrm{Tr}\left[e^{-\beta\hat{H}}\right]$$

It is a key thermodynamic quantity as all thermal averages depend on it.

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- In energy basis with the eigenvalues E_i and corresponding eigenstates $|i\rangle$, the partition function simply reads

$$Z = \mathrm{Tr}[e^{-\beta\hat{H}}] = \sum_i \langle i|e^{-\beta\hat{H}}|i\rangle = \sum_i e^{-\frac{E_i}{k_\mathrm{B}T}}$$

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- With any full and orthonormal basis set $\{\ |j\rangle\ \}$ the partition function Z can be written as a sum over matrix elements of the density operator

$$Z = \mathrm{Tr}[e^{-\beta\hat{H}}] = \sum_i \langle j|e^{-\beta\hat{H}}|j\rangle$$

Results for kinetic and harmonic operators

- Potential energy density matrix in coordinate representation

$$\hat{\mathbf{r}}_i \left|\mathbf{r}\right\rangle = \mathbf{r}_i \left|\mathbf{r}\right\rangle$$

$$\langle R|e^{-\beta\hat{V}}|R'\rangle = \left\langle R \left| e^{-\beta\sum V_{\text{ext}}(\hat{\mathbf{r}}_i)+V_{ij}(\hat{\mathbf{r}}_i,\hat{\mathbf{r}}_j)} \right| R' \right\rangle = e^{-\beta\sum V_{\text{ext}}(\mathbf{r}_i)+V_{ij}(\mathbf{r}_i,\mathbf{r}_j)}\delta(R-R')$$

Definitions: $\lambda_D = 2\pi\hbar(2\pi m k_{\mathrm{B}} T)^{-1/2}$, $|R\rangle = \{\ |\mathbf{r}_1\rangle\ |\mathbf{r}_2\rangle \cdots |\mathbf{r}_N\rangle\ \}$.

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- Kinetic energy density matrix in coordinate representation

$$\hat{\mathbf{p}}_i \left|\mathbf{r}\right\rangle = \int d\mathbf{p}' \, \hat{\mathbf{p}}_i \left|\mathbf{p}'\right\rangle \left\langle \mathbf{p}' | \mathbf{r}\right\rangle$$

$$\langle \mathbf{r} \,|\, \mathbf{p} \rangle = \langle \mathbf{p} | \mathbf{r} \rangle^* = \frac{1}{(2\pi\hbar)^{3/2}} e^{-i\mathbf{r}\cdot\mathbf{p}/\hbar}$$

$$\left\langle R \left| e^{-\beta \hat{K}} \right| R' \right\rangle = \int dP' dP'' \, \langle R \,|\, P' \rangle \left\langle P' \left| e^{-\beta \sum \frac{\hat{\mathbf{p}}_i}{2m_i}} \right| P'' \right\rangle \langle P'' \,|\, R' \rangle$$

$$= \lambda_D^{-3N} e^{-\frac{\pi}{\lambda_D^2}(R_i - R_i')^2}$$

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Density matrix decomposition

- The many-particle Hamiltonian $\hat{H}$ can be written as sum of *kinetic energy operator* $\hat{K}$ and *potential energy operator* $\hat{V}$,

$$\hat{H} = \hat{K} + \hat{V}, \qquad\qquad [\hat{K}, \hat{V}] \neq 0.$$

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- The total density operator $\hat{\rho}$ does not factorize simply:

$$\hat{\rho} = e^{-\beta \hat{H}} = e^{-\beta(\hat{K}+\hat{V})} = e^{-\beta \hat{K}}\, e^{-\beta \hat{V}}\, e^{-(\beta^2 [\hat{K},\hat{V}] + \mathcal{O}(\beta^3))}$$

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  $\hat{\rho}$ is not known in general.

- However, at high temperature (quasi-classical limit) $\beta \longrightarrow 0$, thus:

$$\hat{\rho} = e^{-\beta\hat{H}} = e^{-\beta(\hat{K}+\hat{V})} \longrightarrow e^{-\beta\hat{K}}\, e^{-\beta\hat{V}}$$

  The explicit form of the r.h.s is known. The expressions were listed in coordinate representation on the previous slide. ▸ more

Density matrix decomposition II

- Feynman's idea: Use convolution property of density operator

$$\hat{\rho}(\beta) = e^{-\beta\hat{H}} = \left[e^{-\frac{\beta}{M}\hat{H}}\right]^{M} = [\hat{\rho}(\tau)]^{M}$$

to write the low temperature density operator as a product of high temperature density operators.

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- Using simplest (*first order*) approximation at inverse temperature $\tau = \beta/M$ yields:

$$e^{-\tau(\hat{K}+\hat{V})} = e^{-\tau\hat{K}}\, e^{-\tau\hat{V}}\, e^{\mathcal{O}(1/M)}$$

  We can approximate the density operator with an arbitrarily low error by increasing M.

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  We can approximate the density operator with an arbitrarily low error by increasing M.

- Additionally, there are higher order approximations which reduce the number of factors M needed to achieve the same error. ▸ more

Path-integrals

Rewritting the convolution property for the density matrix in coordinate representation yields

$$\rho(R,R';\beta) = \left\langle R \left| e^{-\beta\hat{H}} \right| R' \right\rangle = \int dR_1 \left\langle R \left| e^{-\frac{\beta}{2}\hat{H}} \right| R_1 \right\rangle \left\langle R_1 \left| e^{-\frac{\beta}{2}\hat{H}} \right| R' \right\rangle$$

$$= \int dR_1 \rho(R,R_1;\beta/2)\rho(R_1,R';\beta/2),$$

Thus, at M-times higher temperature there are $3NM$ additional integrations.

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Discrete time path-integral representation of the density matrix

$$\rho(R,R';\beta) = \int \mathrm{d}R_1\mathrm{d}R_2\ldots\mathrm{d}R_{M-1}\,\rho(R,R_1;\tau)\rho(R_1,R_2;\tau)\cdots\rho(R_{M-1},R';\tau)$$

Common abbrevation:

$$\rho(R,R';\beta) = \int \mathrm{d}R_1\mathrm{d}R_2\ldots\mathrm{d}R_{M-1}\, e^{-\sum_{k=1}^{M} S^k}, \qquad \rho = e^{\ln\rho} \equiv e^{-S}$$

$$S^k = -\ln[\rho(R_{k-1},R_k;\tau)] \approx \ln\left(\lambda_\tau^{d\cdot N}\right) + \frac{\pi}{\lambda_\tau^2}(R_k - R_{k-1})^2 + \tau V(R_k),$$

S^k is called *action*, the r.h.s its primitive approximation.

Path-integral representation

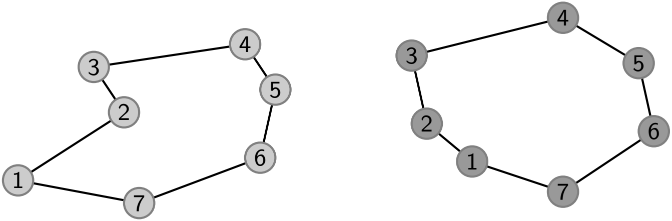

Figure: Two particles represented by set of points. The chain is closed and called a "path" (therefore: "path integral")

Density matrix corresponds to a system of interacting polymers with classical action S:

- "Spring" terms hold polymers (paths) together with typical length $\lambda_\tau^2 = \frac{2\pi\hbar^2\tau}{m}$

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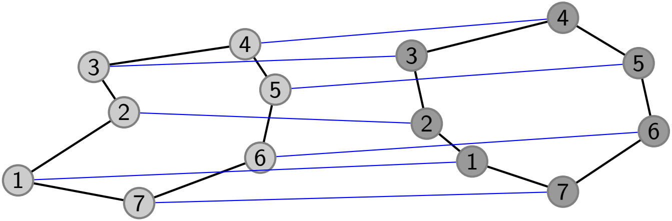

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- Polymer interaction is given by $V_{\text{ext}}(\mathbf{r}_i) + V_{\text{int}}(r_{ij})$

Path-integral representation II

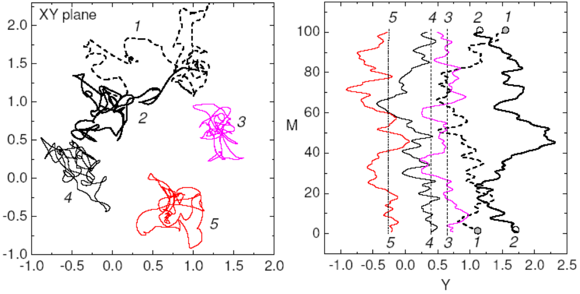

Figure: PIMC results of five particles in a 2D harmonic trap. Left: Snapshot where labels show particles indices. Particles 1 and 2 are the pair exchange. Right: y-component of the paths vs imaginary time $M\tau$.

The term *imaginary time* is used due to the analogy:

- Time propagation operator $e^{-i\hat{H}\tau/\hbar}$
- Density operator $e^{-\beta\hat{H}}$

Density distribution of 2 trapped particles

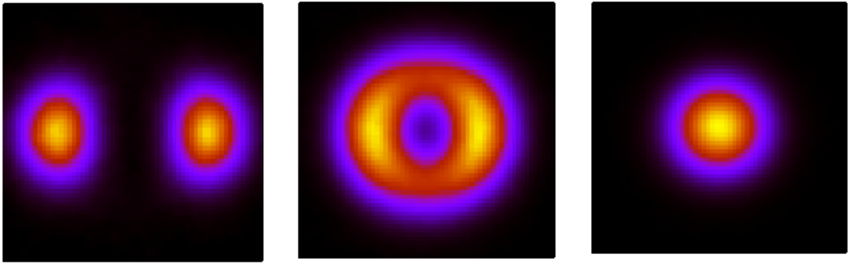

Figure: Averaging over many paths configurations yields smooth probability densities in interacting quantum systems.

Basic numerical issues of PIMC

1. *Sampling of trajectories*:
   it is necessary to explore the whole coordinate space for each intermediate point. This is very time consuming. To speed up convergence: move several slices (points of path) at once.
2. *Construction of more accurate actions*:
   use effective interaction potentials which take into account two, three and higher order correlation effects. More accurate actions help to reduce the number of time slices by a factor of 10 or more.
3. *Estimation of thermodynamic averages*:
   Expectation values of physical observables, e.g. energy, momentum distribution, etc. can be evaluated in different ways called estimators. Convergence can be improved by using an estimator with smaller statistical variance.
4. *Inclusion of quantum statistics*:
   particle statistics (Fermi/Bose) is accounted by proper symmetrization of the density matrix and sampling in the permutation space (direct sampling from $N!$ exchanges only those with non-negligible statistical weights).

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5 Appendix
- Mean-field solutions
- Classical partitial function
- Higher order operator decompositions

Mean-field solutions

Starting point – non-interacting Hartree-Fock wave functions.
We introduce $(\Psi_1, \ldots, \Psi_N)$ – occupied orbitals and $(\Psi_{N+1}, \ldots)$ – virtual orbitals.

$$D_{HF}(\mathbf{r}_1, \ldots, \mathbf{r}_N) = \begin{vmatrix} \Psi_1(\mathbf{r}_1) & \Psi_1(\mathbf{r}_2) & \ldots & \Psi_1(\mathbf{r}_N) \\ \vdots & \vdots & \ddots & \vdots \\ \Psi_N(\mathbf{r}_1) & \Psi_N(\mathbf{r}_2) & \ldots & \Psi_N(\mathbf{r}_N) \end{vmatrix}$$

Spin orbitals: $\Psi_i(\mathbf{r}) = \Phi_i(\mathbf{r})\, \chi_{S_i}(\sigma)$
Spatial part, $\Phi_i(\mathbf{r})$, satisfy HF-equations:

$$\left[-\frac{1}{2}\boldsymbol{\nabla}^2 + V_{ext}(\mathbf{r}) + \sum_{j=1}^{N} \int d\mathbf{r}' \frac{|\Phi_j(\mathbf{r}')|^2}{|\mathbf{r}-\mathbf{r}'|} \right] \Phi_i(\mathbf{r}) + \left[\hat{V}_{HF}\Phi_i \right](\mathbf{r}) = \epsilon_i \Phi_i(\mathbf{r})$$

Now we consider excitations to virtual orbitals: single, double, three, . . . -body excitations

$$\Psi = c_0\, D_{HF} + c_1\, D_1 + c_2\, D_2 + \ldots$$

Goal: Construct more compact form of Ψ.

Partition function: interacting part

◂ back

- Classical partition function:

$$Z = Z_{NVT} \cdot Q_{NVT}^{\text{ideal}} \approx \mathrm{Tr}\left[e^{-\beta \hat{H}}\right]$$

- Configuration integral is the main object of Classical Statistical Mechanics

$$Z_{NVT} = \int d\mathbf{r}^N e^{-\beta V(\mathbf{r}^N)}, \quad R = \mathbf{r}^N = (\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N)$$

  Goal: Evaluate measurable quantities, such as total energy E, potential energy V, pressure P, pair distribution function $g(r)$, etc.

$$\langle A \rangle_{NVT} = 1/Z \int d\mathbf{R}\, A(\mathbf{R})\, e^{-\beta V(\mathbf{R})}, \quad \beta = 1/k_B T$$

  Averaging with the canonical probability distribution (Boltzmann factor) can be performed by the Metropolis algorithm.

- The ideal gas part Q_{NVT}^{ideal} should be treated quantum mechanically but with the known analytical result.

Partition function: ideal gas part

Consider N particles in a box of volume $V = L^3$

$$\epsilon_k = \frac{\hbar^2 \mathbf{k}^2}{2m}, \quad \mathbf{k} = \frac{\pi}{L}(n_x \mathbf{x} + n_y \mathbf{y} + n_z \mathbf{z}),$$

$$\Delta n_x = \frac{L}{\pi} dk_x = \frac{L}{\pi\hbar} dp_x, \quad \sum_{n_x, n_y, n_z} \rightarrow \frac{L^3}{(\pi\hbar)^3} \int_0^\infty d\mathbf{p}$$

$$Q_{NVT}^{\text{ideal}} = \frac{1}{N!} \left(\frac{V}{(2\pi\hbar)^3} \int d\mathbf{p}\; e^{-\beta p^2/2m} \right)^N = \frac{V^N}{N! \lambda_D^{dN}}, \quad \lambda_D^2 = \frac{2\pi\hbar^2\beta}{m}$$

Operator decomposition: higher order schemes

◂ back

- Commutation relations. Baker-Campbell-Hausdorf formula:
  For any pair $\hat{X}$, $\hat{Y}$ of non-commuting operators $[\hat{X}, \hat{Y}] = XY - YX \neq 0$

$$e^{\tau \hat{X}} e^{\tau \hat{Y}} = e^{Z} \tag{1}$$

$$Z = \tau(X+Y) + \frac{\tau^2}{2}[X, Y] + \frac{\tau^3}{12}([X, X, Y] + [Y, Y, X]) + \frac{\tau^4}{24}[X, Y, Y, X] + \mathcal{O}(\tau^5)$$

- Consider now $X = \hat{K}$, $Y = \hat{V}$ and $\tau = \beta/M \ll 1$ $(M \gg 1)$.
  General approach to factorize the exponent

$$e^{\tau(K+V)} = \prod_{j=1}^{n} e^{a_j \tau K} e^{b_j \tau V} + O(\tau^{n+1})$$

  Set of coeff. a_i, b_i are determined by required order of accuracy from Eq. (1).

- Operator decomposition: *n*-order schemes

First order: $e^{\tau(K+V)} = e^{\tau K} e^{\tau V} e^{O(\tau^2)}$

Second order: $e^{\tau(K+V)} = e^{\frac{1}{2}\tau K} e^{\tau V} e^{\frac{1}{2}\tau K} e^{O(\tau^3)}$

Fourth order: $e^{\tau(K+V)} = e^{\frac{1}{6}\tau V} e^{\frac{1}{2}\tau K} e^{\frac{1}{6}\tau \tilde{V}} e^{\frac{1}{2}\tau K} e^{\frac{1}{6}\tau V} e^{O(\tau^5)}$,

$\tilde{V} = V + \dfrac{1}{48}\tau^2[V, [K, V]]$ - correction to classical potential