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The partial averaging Fourier path Integral approach based on the harmonic reference path

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Abstract. The Monte Carlo Fourier path integral approach has proved to be quite useful in calculating equilibrium thermodynamic properties. One of its advantages is that it can be formulated in such a way as to include higher order terms using the partial averaging technique, which includes the contribution from higher terms usually neglected by the discretized path integral approach. In the original approach, the Feynman path integral is evaluated via a free-particle reference state. Here, using a new expression for the Feynman paths expanded around a harmonic reference path, we derive an alternative formulation for the density matrix element and its corresponding partial averaging expression.

Key words: Path integral – Free energy

1 Introduction

Feynman path integral methods are quite useful in calculating equilibrium thermodynamic properties such as density matrix elements, partition functions and other equilibrium thermodynamical properties [1–10]. Generally, there are two kinds of approach to calculating path integrals. One approximation, referred to as the discretized path integral (DPI) approach, is to discretize the quantum paths such that the quantum particle becomes isomorphic to a chain of p classical beads connected with each other through a temperature-dependent harmonic force [2, 3, 5, 11]. Another approach, called the Fourier path integral (FPI) approach, is to expand the quantum path into a Fourier series [1, 12] and to use only the first p low-order terms in numerical calculations. These approximations usually give accurate and converged results for cases at relatively high temperature, where small p will usually suffice. However, at low temperature these approximations start to suffer from slow convergence, because larger p is required. In the framework of both approaches, many methods [13–22] were introduced, using improved propagators, better reference systems or better sampling techniques, to accelerate the convergence at low temperature; however these approaches still drop off the terms or beads presumed to have a negligible contribution.

The Monte Carlo FPI approach was introduced by Doll and Freeman [12]. Though the truncated version of the FPI approach, where the higher order terms are left out, is essentially comparable to the DPI method [10, 15] in terms of convergence, the former is advantageous over the latter in that the FPI method, by means of partial averaging (PA) [1, 6, 7, 9, 10, 23, 24], can include the average effects of the higher order terms that are left out in other approaches, i.e., the truncated FPI or the DPI methods. In the original FPI approach, the quantum path is expanded around a free-particle path (FP) by a Fourier expansion; hence, it is expected that a reference system other than the free-particle system should further improve the PA FPI calculations. PA FPI approaches [6, 7, 9, 24] were indeed proposed based on variational or local harmonic reference states; however all these approaches are based on the centroid formulation [1], so they cannot be used to calculate thermal propagators or density matrix elements. In the present work, starting from the original FPI thermal propagator, we have derived an alternative harmonic-referenced PA FPI formulation for the thermal propagator and its corresponding PA version, and we demonstrate its applicability to a model system at low temperature.

2 Methods

In the original FPI formulation [12], the path is expanded in a Fourier series around the free–particle reference path, i.e.,

$$x(\tau) = x_{\mathrm{fp}}(\tau) + \sum_{n=1}^{\infty} a_n \sin(\Omega_n \tau) \ , \tag{1}$$

where x_{fp} is a FP given by $x_i + (x_f - x_i)\tau/\hbar\beta$, with x_i and x_f denoting the initial and final positions, β is $1/k_{\mathrm{B}}T$, k_{B} is the Boltzmann constant and T is temperature, and $\Omega_n = n\pi/\hbar\beta$. With this repre-

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sentation of the Feynman paths, the thermal propagator or density matrix element can be written as

$$\rho(x_f,x_i)=\rho_{\rm fp}(x_f,x_i)\times\left\langle\exp\left(-\frac{1}{\hbar}\int_0^{\beta\hbar}d\tau V[x(\tau)]\right)\right\rangle_{a_1\ldots a_\infty}, \tag{2}$$

where $\rho_{\rm fp}(x_f,x_i)$ is the free-particle density matrix element given by,

$$\rho_{\rm fp}(x_f,x_i)=\frac{1}{\sqrt{2\pi\hbar^2\beta/m}}\exp\left[-\frac{m}{2\hbar^2\beta}(x_f-x_i)^2\right] \tag{3}$$

and the notation $\langle\cdots\rangle_{a_1,\ldots,a_\infty}$ in Eq. (2) indicates a Gaussian average over the Fourier coefficients (a_i),

$$\langle\cdots\rangle_{a_1,\ldots,a_\infty}=\int\frac{da_1\ldots da_\infty}{\prod_{n=1}^\infty\sqrt{2\pi s_n^2}}\exp\left(-\sum_{n=1}^\infty\frac{a_n^2}{2s_n^2}\right)\exp\left(-\frac{1}{\hbar}\int_0^{\beta\hbar}d\tau V[x(\tau)]\right) \tag{4}$$

with the Gaussian widths s_n given by $s_n^2=2/m\beta\Omega_n^2$. For convenience, we shall refer to this approach as the FP method. In the truncated version of the FP approach, only the first p terms are used, while the higher order coefficients are neglected. The truncated FPI is then calculated by the Monte Carlo method.

In the PA FP approach, the higher order terms, instead of being just thrown out, are included in an average way by means of a PA technique [10, 23]. The PA FP thermal propagator is given by

$$\rho(x_f,x_i)\sim\rho_{\rm fp}(x_f,x_i)\left\langle\exp\left(-\frac{1}{\hbar}\int_0^{\beta\hbar}d\tau\tilde V[\bar x_{\rm fp}(\tau)]\right)\right\rangle_{a_1,\ldots,a_p}, \tag{5}$$

where the effective potential $\tilde V[\bar x_{\rm fp}(\tau)]$ is

$$\tilde V[\bar x_{\rm fp}(\tau)]=\int dyV(q+\bar x_{\rm fp})\frac{\exp\left(-y^2/2\alpha_{\rm fp}^2\right)}{\sqrt{2\pi\alpha_{\rm fp}^2}} \tag{6}$$

and the truncated path $\bar x_{\rm fp}(\tau)$ and the Gaussian width $\alpha_{\rm fp}$ are given by

$$\bar x_{\rm fp}(\tau)=x_{\rm fp}(\tau)+\sum_{n=1}^p b_n\sin(\Omega_n\tau) \tag{7}$$

$$\alpha_{\rm fp}^2=\frac{1}{m\beta}\tau(\hbar\beta-\tau)-\sum_{n=1}^p s_n^2\sin^2\Omega_n\tau\ . \tag{8}$$

The PA FP approach has been shown to be very powerful, with only a moderate number of Fourier terms, in calculating thermodynamical properties at low temperature [10, 23].

We start from Eq. (2), inserting a reference potential $V_0(x)$, and obtain

$$\rho(x_f,x_i)=\rho_{\rm fp}(x_f,x_i)\left\langle\exp\left(-\frac{1}{\hbar}\int_0^{\beta\hbar}d\tau V_0[x(\tau)]\right)\times\exp\left(-\frac{1}{\hbar}\int_0^{\beta\hbar}d\tau[V[x(\tau)]-V_0[x(\tau)]]\right)\right\rangle_{a_1\ldots a_\infty}. \tag{9}$$

In the case of $V_0(x)=\frac{1}{2}m\omega^2x^2$, the integral of $V_0[x(\tau)]$ over τ can be evaluated analytically, i.e.,

$$\int_0^{\beta\hbar}d\tau V_0[x(\tau)]=\hbar\beta m\omega^2\left[\frac{1}{6}\left(x_i^2+x_ix_f+x_f^2\right)+\sum_{n=1}^\infty\frac{a_n^2}{4}+\sum_{n=1}^\infty\frac{[x_i-(-1)^nx_f]}{\pi n}a_n\right]. \tag{10}$$

Substituting Eq. (10) into Eq. (9), and using the identity

$$\prod_1^\infty\sqrt{\frac{\Omega_n^2}{\Omega_n^2+\omega^2}}=\sqrt{\frac{\hbar\omega\beta}{\sinh\hbar\omega\beta}}\ , \tag{11}$$

we obtain a very simple expression for the thermal propagator,

$$\rho(x_f,x_i)=\rho_{\rm hmo}(x_f,x_i)\left\langle\exp\left(-\frac{1}{\hbar}\int_0^{\beta\hbar}d\tau\delta V[x(\tau)]\right)\right\rangle_{b_1\ldots b_\infty}, \tag{12}$$

which is similar in appearance to Eq. (2). Here $\rho_{\rm hmo}$ is the harmonic density matrix element:

$$\rho_{\rm hmo}(x_f,x_i)=\frac{1}{\sqrt{2\pi\hbar^2\beta/m}}\sqrt{\frac{\hbar\omega\beta}{\sinh\hbar\omega\beta}}\times\exp\left[\frac{m\omega}{\hbar}\left(\frac{x_ix_f}{\sinh\hbar\omega\beta}-\frac{\left(x_i^2+x_f^2\right)}{2}\coth\hbar\omega\beta\right)\right] \tag{13}$$

and $\delta V(x)=V(x)-\frac{1}{2}m\omega^2x^2$. The Gaussian average $\langle\cdots\rangle_{b_1\ldots b_\infty}$, with widths $\sigma_n^2=2/m\beta(\Omega_n^2+\omega^2)$, is now averaged over a new set of variables b_n, which is related to a_n through the following relationship

$$b_n=a_n+\frac{2\omega^2}{\pi}\frac{[x_i-(-1)^nx_f]}{n(\Omega_n^2+\omega^2)}\ . \tag{14}$$

In terms of b_n, the quantum path is of the following form,

$$x(\tau)=\left[x_i+(x_f-x_i)\tau/\hbar\beta-\sum_{n=1}^\infty\frac{2\omega^2}{\pi}\frac{(x_i-(-1)^nx_f)}{n(\omega^2+\Omega_n^2)}\sin(\Omega_n\tau)\right]+\sum_{n=1}^\infty b_n\sin(\Omega_n\tau)\ . \tag{15}$$

The seemingly complicated terms inside the brackets of Eq. (15) can reduce to a simple, suggestive form,

$$[\cdots]=\frac{1}{\sinh\hbar\omega\beta}\left[x_f\sinh\omega\tau-x_i\sinh(\omega\tau-\hbar\omega\beta)\right]\ . \tag{16}$$

Immediately, we see that Eq. (16) is actually the trajectory of a harmonic oscillator that propagates in imaginary time and satisfies the boundary conditions: $x(0)=x_i$ and $x(\hbar\beta)=x_f$. It is clear that Eq. (15) gives the expression for the quantum path expanded around a harmonic path, i.e., Eq. (16), in terms of b_n. For convenience, we will designate the harmonic path as $x_{\rm hmo}(\tau)$, and refer to our approach (Eqs. 12, 15 and 16) as the harmonic path (HP) approach.

Typical Feynman paths expanded in FP and HP series, i.e., Eqs. (1) and (15), are plotted in Fig. 1. The paths with $p=0$ and $p=250$ are drawn as the solid line and the dotted line, respectively. All paths plotted are closed, i.e., the initial point is identical to the final point of the path. It is interesting to note that the paths based on the harmonic reference state (Fig.1a) will approach $x=0$ at $\tau=\hbar\beta/2$ with fluctuations introduced by the higher order terms ($p\neq0$). The paths based on the free-particle reference state (Fig. 2a) fluctuate around the straight line traced by the free particle. In the limit of large p, these representations of the Feynman paths become identical, as expected. In the limit of ω approaching zero, the HP Gaussian width σ_n reduces to the FP Gaussian width s_n. Equations (12), (15) and (16) offer an alternative formulation for the FPI calculation of the thermal propagator. In the case of diagonal density matrix elements, the frequency ω can be conveniently taken to be the second derivative of the potential, $d^2V(x)/dx^2$; however, in the case of the off-diagonal matrix elements, the choice of the frequency is not unique. One of the options is to use the second derivative of the potential function at either x_i or x_f, or even the midpoint $(x_i+x_f)/2$. In the case of negative second derivatives such as double-well potentials, the terms involving the denominator $\Omega_n^2+\omega^2$ could become zero or negative. This presents no problem, since we can always choose a value of ω such that $\Omega_n^2+\omega^2$ is greater than zero and Eq. (12) can be evaluated by the usual Monte Carlo method.

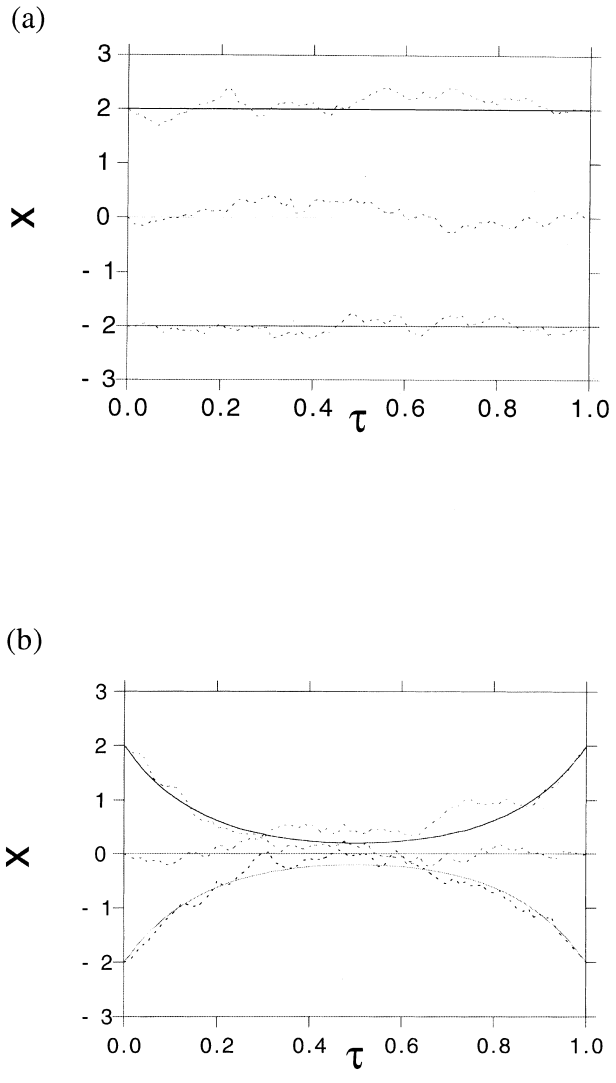

Fig. 1. Comparison of **a** the harmonic reference paths (**HP**) and **b** the free-particle reference paths (**FP**). All paths plotted are closed, i.e., the initial point is identical to the final point of the path. The *solid lines* are the paths with $p = 0$, and the *dotted lines* are the paths with $p = 250$

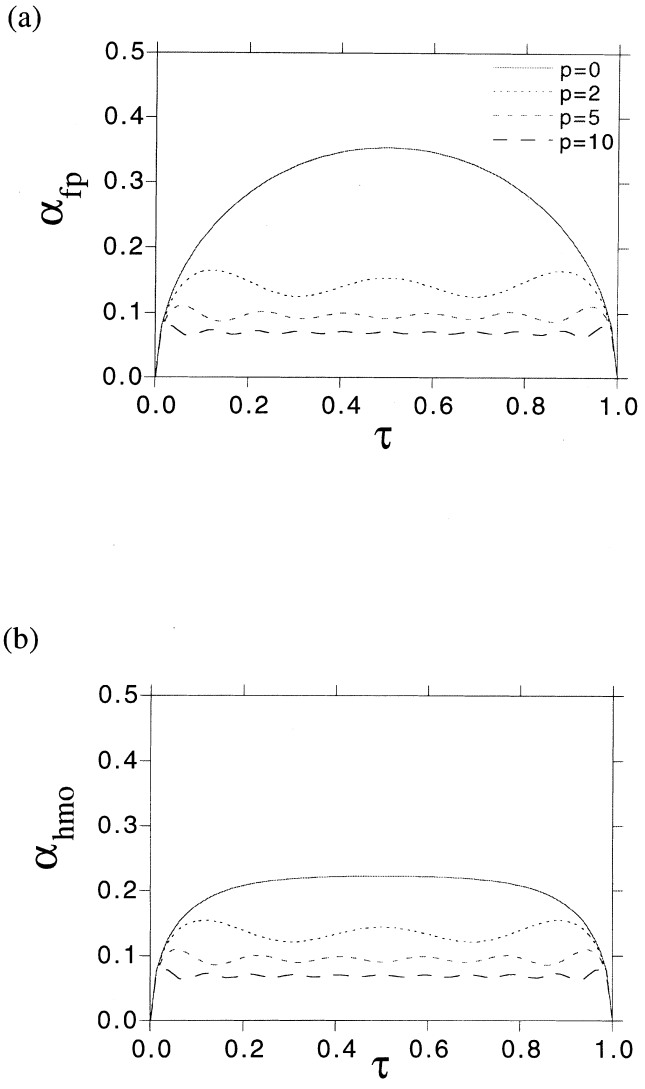

Fig. 2. Comparison of the Gaussian widths **a** α_{hmo} and **b** α_{fp} as a function of τ (in units of $\hbar\beta$)

3 The PA implementation

The implementation of PA to the HP formulation is rather straightforward [10, 23], and the final PA expression for the FP thermal propagator is,

$$\rho(x_f, x_i) \sim \prod_{n=1}^{p} \sqrt{\frac{\Omega_n^2 + \omega^2}{\Omega_n^2}} \times \exp\left(-\sum_{1}^{p} \frac{\beta m \omega^4 \left[x_i + (-1)^{n+1} x_f \right]^2}{n^2 \pi^2 \left(\omega^2 + \Omega_n^2 \right)} \right) \times \rho_{\mathrm{hmo}}(x_f, x_i) \times \left\langle \exp\left(-\frac{1}{\hbar} \int_0^{\beta\hbar} d\tau \delta \tilde{V}[\bar{x}_{\mathrm{hmo}}(\tau)] \right) \right\rangle_{b_1, \ldots, b_p} . \tag{17}$$

Here $\bar{x}_{\mathrm{hmo}}(\tau)$ is the truncated path with terms up to order p:

$$\bar{x}_{\mathrm{hmo}}(\tau) = x_{\mathrm{hmo}}(\tau) + \sum_{n=1}^{p} b_n \sin(\Omega_n \tau) \tag{18}$$

and the effective potential $\delta\tilde{V}[\bar{x}(\tau)]$ is given by

$$\delta \tilde{V}[\bar{x}_{\mathrm{hmo}}(\tau)] = \int dy \delta V(y + \bar{x}_{\mathrm{hmo}}) \frac{\exp\left(-y^2/2\alpha_{\mathrm{hmo}}^2\right)}{\sqrt{2\pi\alpha_{\mathrm{hmo}}^2}} . \tag{19}$$

The Gaussian width α_{hmo} is given by,

$$\alpha_{\mathrm{hmo}}^2 = \frac{\hbar}{2m\omega} \frac{\cosh \hbar\omega\beta - \cosh(\hbar\omega\beta - 2\omega\tau)}{\sinh \hbar\omega\beta} - \sum_{n=1}^{p} \sigma_n^2 \sin^2 \Omega_n \tau . \tag{20}$$

In the limit $\omega \to 0$, it is not hard to see that Eqs. (17)–(20) reduce to Eqs. (5)–(8). The Gaussian widths α_{hmo}

and $\alpha_{\rm fp}$ as a function of τ are compared in Fig. 2. They show quite distinct shapes at $p = 0$, but when p increases they become similar.

The multidimensional implementation of the HP method is rather straightforward [9]. The N-dimensional version of the smeared potential $\tilde{V}[\mathbf{x}_p(\tau)]$ is given by

$$\tilde{V}[\mathbf{x}_p(\tau)] = \int \prod_i^N \frac{dx_i}{\sqrt{2\pi\alpha_i^2}} \times \exp\left(-\sum_{j=1}^N \frac{\xi_j^2}{2\alpha_j^2}\right) V\left[\mathbf{x} + \mathbf{x}_p(\tau)\right] \ , \tag{21}$$

where the mass-weighted coordinates x_i are used here. In practical calculations, Eq. (21) can be expanded in a Taylor series,

$$\tilde{V}(\mathbf{x}) \approx V(\mathbf{x}) + \frac{1}{2}\sum_i^N \left(\frac{\alpha_i^2}{2}\right) V_{x_i x_i} + \cdots \ , \tag{21}$$

where $V_{x_i x_i} = \partial^2 V/\partial x_i \partial x_i$. The quantities ξ_j and α_j^2 in Eq. (21) are given by

$$\xi_j = \sum_{k=1}^N x_j C_{jk}$$

$$\alpha_j^2 = \frac{\hbar}{2\omega_j} \frac{\cosh \hbar\omega_j\beta - \cosh\left(\hbar\omega_j\beta - 2\omega_j\tau\right)}{\sinh \hbar\omega_j\beta} - \sum_{n=1}^p \sigma_{jn}^2 \sin^2 \Omega_n \tau \ . \tag{22}$$

Here the Gaussian width σ_{jn}^2 is given by $\sigma_{jn}^2 = 2/\beta\left(\Omega_n^2 + \omega_j^2\right)$. The quantities ω_j and C_{jk} are the jth eigenvalue and its corresponding kth eigenvector, respectively, of the $N \times N$ matrix F defined by

$$F_{ij} = \frac{1}{\hbar\beta\sqrt{m_i m_j}} \int_0^{\hbar\beta} d\tau \tilde{V}_{x_i x_j}\left[\mathbf{x}_p(\tau)\right] \ , \tag{23}$$

where $V_{x_i x_j} = \partial^2 V/\partial x_i \partial x_j$.

4 Results and discussion

Consider a well-known model system: a harmonic oscillator coupled with a quartic term through g,

$$V(x) = \frac{1}{2}x^2 + \frac{g}{4}x^4 \ . \tag{24}$$

The effective potential can be solved analytically,

$$\tilde{V}(x) = \frac{1}{2}\left(x^2 + \alpha^2\right) + \frac{g}{4}\left(x^4 + 6x^2\alpha^2 + 3\alpha^4\right) \ ,$$

where α is the Gaussian width. For convenience, we will set both m and $\hbar$ to 1. In most cases, it is difficult to obtain analytical solutions for the effective potential, and the following expansion should be useful,

$$\tilde{V}\left(\bar{x}_p\right) = \sum_{n=0}^\infty \frac{1}{n!}\left(\frac{\alpha^2}{2}\right)^n V^{(2n)}\left(\bar{x}_p\right) \tag{25}$$

where the superscript $(2n)$ denotes the $2n$th derivative. The diagonal density matrix elements, calculated by the FP and HP approaches are plotted in Fig. 3. As shown in the figure, the HP methods give better results than the FP methods, and the density matrix elements calculated by the PA FP method with $p = 4$ are almost indistinguishable from the exact values. The convergence of the quantum free energy calculated by the FP and HP approaches is compared in Fig. 4. As expected, the HP methods perform better. It is interesting to note that at small p, the truncated HP method gives better results than the PA FP method, but the latter quickly outperforms the former as p increases. In general, both HP methods, either discreted or partial averaged, give better results than the corresponding FP approaches.

In summary, using a new expression for the Feynman paths expanded around a harmonic reference path, we have derived an alternative FPI expression for the den-

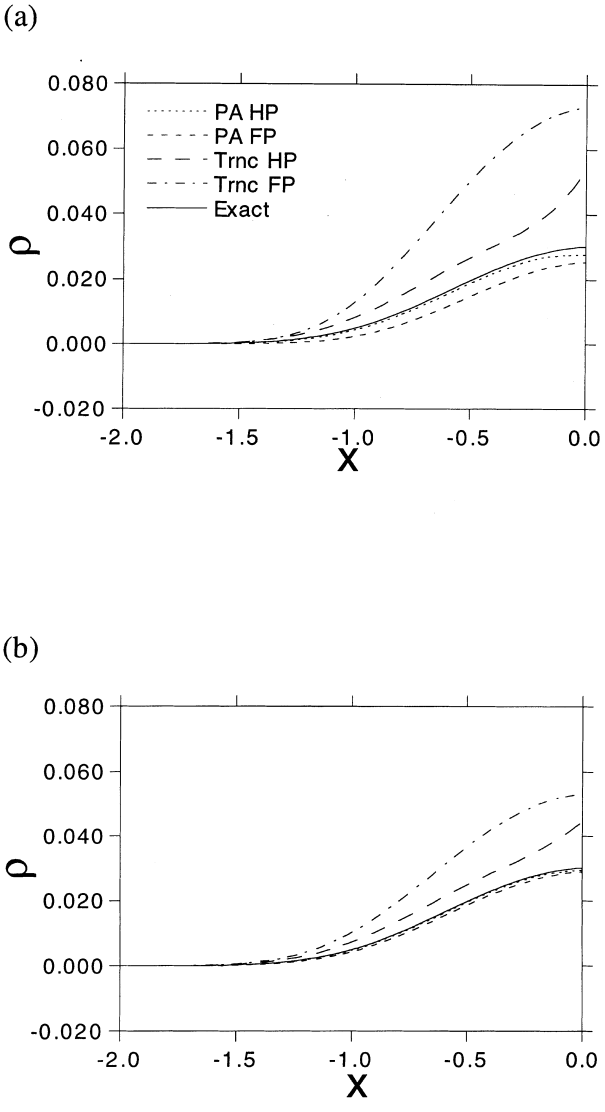

Fig. 3a, b. Comparison of the convergence of the diagonal density matrix elements $\rho(x)$ calculated by various Monte Carlo Fourier path integral (MC FPI) methods. The number of Fourier terms p is 2 in **a** and 4 in **b**. The parameters for the system (Eq. 18) are: $g = 10$ and $\beta = 4$. partial averaging (PA), truncated (Trnc)

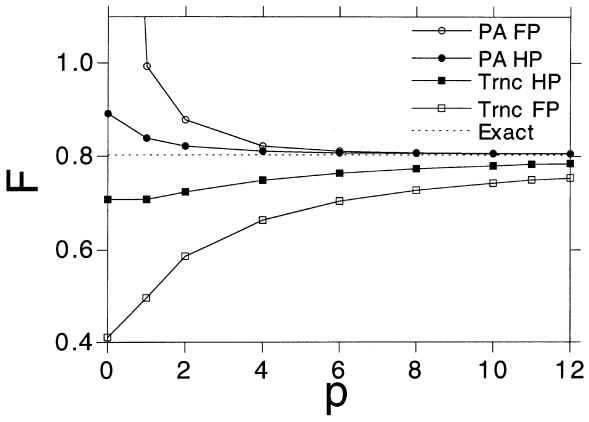

Fig. 4. The quantum free energy as a function of p, calculated by various MC FPI methods. The parameters of the system are the same as those in Fig. 3

sity matrix element, in both the truncated and PA forms. This new formulation performs satisfactorily in the calculation of the thermal propagator and the quantum free energy.

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