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ARTICLES

Wavelet formulation of path integral Monte Carlo

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A wavelet formulation of path integral Monte Carlo (PIMC) is constructed. Comparison with Fourier path integral Monte Carlo is presented using simple one-dimensional examples. Wavelet path integral Monte Carlo exhibits a few advantages over previous methods for PIMC. The efficiency of the current method is at least comparable to other techniques. © 2002 American Institute of Physics. [DOI: 10.1063/1.1504439]

I. INTRODUCTION

Path integral Monte Carlo (PIMC)¹ combines the conceptual clarity in linking quantum mechanics to classical Lagrangian dynamics (path integral)² with computational power of Monte Carlo sampling method.³ There have been two different approaches to incorporating Monte Carlo sampling into path integral formalism. One is discretized path integral (DPI) Monte Carlo;⁴ the other is Fourier path integral (FPI) Monte Carlo.^{2,5} These two methods are proven to exhibit similar numerical behavior by Coalson, who established an intimate connection between them by rewriting the DPI formulation in a Fourier-type way.⁶ Even with fundamental connections between these methods, each has some advantages and disadvantages of its own.

Wavelet theory is a natural extension of Fourier analysis, and has been used in many of engineering and physics disciplines for its ability to compress data greatly. Unlike plane waves, which are a basis for Fourier analysis, wavelets are localized in both time and position. For this reason, wavelets are better suited for describing abrupt changes in signals. What made wavelets such a big success is the discovery of the algorithm called fast wavelet transform (FWT) which is analogous to fast Fourier transform (FFT). Using iterative arguments, Daubechies⁷ was able to produce a family of wavelets that are, in basis form, orthonormal.

Wavelet theory had been used in engineering fields even before the term was coined. Physicists soon caught up with this theory and applied it to physical applications. For example in electronic structure theory, Cho *et al.*⁸ first employed wavelet theory in solving Schrödinger equation for hydrogenlike atoms and H_2^+ containing one electron and obtained a good description of the wave function and eigenvalue. Their work utilized Mexican hat wavelet to generate a tight frame and represents an extension of multiresolution analysis to nonorthogonal bases. Though it turned out that this particular basis set of Gaussian scaling function and

Mexican hat wavelet is well suited for the representation of the electronic wave functions due to their smoothness, the lack of an FWT for these nonorthogonal bases reduces their overall utility. Following this application of wavelet theory to electronic structure calculation, several other researchers used orthonormal wavelet bases in self-consistent calculation and molecular dynamics calculation.^{9,10}

It is natural to ask, given all these developments, whether it is possible to combine wavelet expansion with PIMC. Consider a one-dimensional box potential with infinite walls. Suppose further that there exist barriers around the center of the box. A quantum particle placed at the center can sometimes cross over the barriers and experiences hard repulsions from the walls. A typical path of such motion could be described as having “abrupt” peaks along a straight line (Fig. 1). One can view such paths as “signals” following signal processing language. Then the “signal” in the figure can be described with wavelets more efficiently than with Fourier series as shown in the practice of signal processing due to its localized variations. Hence, we expect that this combination of wavelet expansion with PIMC, which uses wavelets to represent the paths might provide a more compact representation of the important paths in the problem.

In this paper, we formulate wavelet path integral Monte Carlo (WPIMC). We start with a brief introduction to wavelet theory, which is followed by a formal discussion on the formulation. As an illustration, simple model problems are solved with WPIMC and numerical results are compared with other methods, particularly FPI. Finally, we conclude with the findings of this endeavor and future direction of research.

II. WAVELET THEORY

There are an infinite number of different wavelets. Among these, we restrict our discussion to orthonormal compact wavelets with fast wavelet transform (FWT). Wavelets are basis for expanding square-integrable (L^2) function space, much like plane waves in Fourier analysis. Although wavelets can be thought of as physical functions in configu-

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FIG. 1. A typical path of a particle in one-dimensional box potential with barriers. The particle mostly stays at the center where the potential is zero but occasionally “tunnels” through the barriers and bounces off the infinite walls so that the paths contains narrow, cuspy “spikes.”

ration space, owing to their development by work of Mallat,^{11,12} one can construct “wavelet filters,” which translate directly into wavelet transforms without any reference to wavelets themselves.

Wavelet transform comes from the concept of multiresolution analysis (MRA). In MRA, one applies a pair of complementing filters recursively to smooth out a given signal. Let us give a formal definition of MRA in the following.

Consider the space of square-integrable functions defined on $\mathbb{R}$, $L^2(\mathbb{R})$. We are attempting to set up a sequence of subspaces of $L^2(\mathbb{R})$ which represent successive approximations to $L^2(\mathbb{R})$. Consider a subspace V_0 , which we assume has an orthonormal basis $\{\phi(x-n); n \in \mathbb{Z}\}$, consisting of a “localized” function ϕ centered at evenly spaced grid points. Then we can construct a “finer” subspace V_1 , which has an orthonormal basis $\{\phi(2x-n); n \in \mathbb{Z}\}$. The grid size in V_1 is reduced by 1/2. In a similar fashion, we can construct a “coarser” subspace V_{-1} , spanned by $\{\phi(x/2-n); n \in \mathbb{Z}\}$. Working recursively in both directions, we define a sequence of subspaces V_j , which corresponds to finer scales as j increases. By choosing an appropriate ϕ , it is possible to have $V_{j-1} \subset V_j$ and $\lim_{j \rightarrow \infty} V_j = L^2(\mathbb{R})$. The function ϕ is called a scaling function. Since $\phi(x) \in V_0 \subset V_1$, we can express $\phi(x)$ in terms of basis functions in V_1 :

$$\phi(x) = \sqrt{2} \sum_n h_n \phi(2x-n). \quad (1)$$

This dilation equation relates the basis functions from different scales. The scalars $\{h_n\}$ are called the dilation coefficients that characterize ϕ . It follows that if $\{\phi(x-n); n \in \mathbb{Z}\}$ is an orthonormal basis for V_0 , $\{\phi_{j,n}(x-n) = 2^{j/2} \phi(2^j x - n); n \in \mathbb{Z}\}$ is an orthonormal basis for V_j . One can then use these subspaces to approximate general functions. For every $j \in \mathbb{Z}$, we can define the space W_{j-1} to be the orthogonal complement of V_{j-1} in V_j , such that

$$V_j = V_{j-1} \oplus W_{j-1}. \quad (2)$$

Applying this decomposition recursively, we have

$$V_j = V_0 \oplus \bigoplus_{k=0}^{j-1} W_k. \quad (3)$$

Now, there exists a function ψ so that $\{\psi(x-n); n \in \mathbb{Z}\}$ is an orthonormal basis for W_0 . It follows again, that $\{\psi_{j,n}(x) = 2^{j/2} \psi(2^j x - n); n \in \mathbb{Z}\}$ forms an orthonormal basis for W_j . We call this function ψ a wavelet. When j is taken to be infinite, V_j becomes dense in $L^2(\mathbb{R})$ and thus we can express any function in $L^2(\mathbb{R})$ with a linear combination of the scaling function and wavelets. Extending Eq. (3) to infinity in the other direction, one also obtains

$$L^2(\mathbb{R}) = \bigoplus_{k=-\infty}^{\infty} W_k, \quad (4)$$

which forms an orthonormal basis in $L^2(\mathbb{R})$. The linear transform between the coefficients of basis in V_j and the coefficients of basis in the right-hand side of Eq. (3) is called the discrete wavelet transform (DWT).

One class of wavelets that stems from MRA is Daubechies wavelet. When plotted, the values of Daubechies wavelets are nonzero only on finite and closed intervals (compact support). Having compact support can be important especially when one adopts numerical methods. Without this property, one has to truncate the “tails” of the wavelets and thus introduces unwanted errors. There are an infinite number of Daubechies wavelets, which are labeled by “order.” Daubechies wavelets can only be generated by an iterative algorithm and the order is related to the number of coefficients used in the corresponding DWT. Loosely speaking, higher order Daubechies wavelets are “smoother” and have larger support. In general, one can express an expansion of function $f(x)$ by Daubechies wavelets as the following:

$$f(x) = c_0 \phi(x) + \sum_{j=1}^{\infty} \sum_{k=1}^{2^j-1} c_{j,k} \psi_{j,k}(x). \quad (5)$$

$\phi(x)$ is called a scaling function. As we show in the discussion of MRA, in an orthonormal wavelet expansion, we only

need to include the lowest order scaling function and hence we set the index of the coefficient for the scaling function as c_0 . $\psi_{j,k}$'s in the double sum are called the wavelets. They are labeled with two indices. The first index j indicates the resolution level, and corresponds to finer resolution with increasing value. The second index k is dependent on j , running from 1 to $2j-1$. There are $2j-1$ wavelets at the given level with index j , and k is the index for these wavelets with resolution level j depending on the position. $c_{j,k}$'s are the coefficients for corresponding wavelets.

III. FORMULATION

For a review on Fourier path integral Monte Carlo, readers are referred to an article by Doll *et al.*⁵ Here, we merely display the representation of paths using Fourier terms as used in the original formulation of FPI:

$$x(u) = x + (x' - x)u + \sum_{k=1}^{\infty} a_k \sin(k\pi u), \quad (6)$$

where the time variable u is defined by $u = \tau/\beta\hbar$ and runs from 0 to 1. To formulate WPIMC, we need to consider the representation of paths including wavelet expansion, which was introduced in an earlier section. Mimicking FPI's representation of paths, we write

$$x(u) = x + (x' - x)u + s_0\phi(u) + \sum_{j=1}^{\infty} \sum_{k=1}^{2j-1} w_{j,k}\psi_{j,k}(u) + (\alpha u + \delta). \quad (7)$$

As in FPI, u varies from 0 to 1 so that the initial position is x and the final position x' . Just as in Eq. (6), we are expressing the fluctuations around the straight line with wavelet terms. A wavelet that is associated with the multiresolution analysis (MRA) does not have to be compactly supported. In fact, as long as one truncates the scaling function and wavelets in Eq. (7) so that they do not extend out of $0 \leq u \leq 1$, the boundary condition of initial and final position would be satisfied. Nonetheless, using a compactly supported wavelets eliminates the truncation error resulting from using noncompact wavelets, and we also have FWT algorithm¹³ for Daubechies wavelets readily available. Thus, we maintain our restriction to Daubechies wavelets for the choice of wavelets in Eq. (7). The support of Daubechies wavelet of order N is the interval $[0, 2N-1]$. This means that for $N \geq 2$, the "tail" of the first few wavelets will spill over the interval $[0, 1]$, in which we are interested. For the routines we used, this fact reveals itself through "wrapped-around tail error." To compensate this discrepancy, we add the linear term $\alpha u + \delta$ at the end of the expression. The constants α and δ are adjusted after the inverse wavelet transformation to "level" and "zero" the fluctuation terms. Since the wavelet expansion can describe any function that is $L^2[0,1]$, this addition of linear terms should not affect the completeness of this expression.

There is one more boundary condition to worry about. If we integrate both sides of Eq. (6) with respect to u , we see that

$$\langle x \rangle = \frac{1}{2}(x' + x) + \sum_{k \text{ odd}} \frac{2a_k}{k\pi}, \quad (8)$$

where $\langle x \rangle$ means the average over $u \in [0,1]$. The interpretation of this result is trivial. The average value of x over the given interval is just the arithmetic mean of the initial and final positions (straight line contribution) plus the odd sine functions contribution. This will give us the ability to exploit nonsymmetric deviation when we are looking at the motion of particles that start and end at the origin. How about the case of wavelet expression? A quick inspection may lead to a contradiction that since all the wavelets would integrate to zero, there is no way that one can guide the position average to nonzero value. It is the scaling function that saves our day, and the wavelet analogue of Eq. (8) is given by

$$\langle x \rangle = \frac{1}{2}(x' + x) + s_0 + \frac{1}{2}\alpha + \delta. \quad (9)$$

It is clear now that the compactly supported orthogonal wavelets can be combined to describe any paths that start at x and end at x' .

With this description of paths, we are ready to write down the action integral for WPIMC. From Doll *et al.*⁵ we have the expression for imaginary time path integral action:

$$S[x(\tau)] = \frac{1}{\hbar} \int_0^{\beta\hbar} d\tau \left\{ \frac{m}{2} \left(\frac{dx(\tau)}{d\tau} \right)^2 + V[x(\tau)] \right\}. \quad (10)$$

We simply substitute x in (10) with the expression (7):

$$S[x(u)] = \beta \int_0^1 du \left\{ \frac{m}{2\beta^2\hbar^2} \left((x' - x) + \alpha + s_0\phi'(u) + \sum_{j,k} w_{j,k}\psi'_{j,k}(u) \right)^2 + V[x(u)] \right\}. \quad (11)$$

Unlike FPI, the kinetic term cannot be evaluated analytically, and the numerical differentiation and integration must be used. Once the integration is completed, we have an expression for the action in terms of x' , x and the wavelet coefficients. For the simplicity of notation, let us include s_0 , as a special case of $w_{j,k}$, say, w_s , in a vector notation $\vec{w}$ for wavelet coefficients.

An average of an operator A then can be written as

$$\langle A \rangle = \frac{\int dx d\vec{w} \exp(-S(x, \vec{w})) A(x)}{\int dx d\vec{w} \exp(-S(x, \vec{w}))}. \quad (12)$$

Again, as long as we consider an average of quantities of interest and not the individual density matrix elements, we do not have to worry about the Jacobian for our change of variables.

Some words on comparison with FPI are in order. In FPI, the kinetic terms in action integral are reduced to squares of Fourier coefficients after integration with time variable and thus action integral evaluation during the course of simulation can be done easily. In WPIMC, we do not have that luxury and the integral has to be done numerically. There is a slight catch-up in this case, however, since doing the action integral with both kinetic and potential term together would not be twice as much as doing the potential term integral alone, which in FPI, one must do. Naturally, in WPIMC, just like in FPI, one must truncate the number of

wavelet terms to be included to finite number. However, there is a difference here. In FPI one can stop counting Fourier terms at any number. In WPIMC on the other hand, since at each level of resolution the number of wavelets varies and one must use all the wavelets at the given level of resolution, one needs all the basis for the given space. Consequently, the number of wavelet terms to be included must be an integer power of 2. This condition is better termed as a restriction on index j , not on k in Eq. (7).

IV. IMPLEMENTATION

In order to put this formalism into actual simulations, a few things must be considered. First of all, in Eq. (11) we see that the derivatives of wavelets appear. There is no trick, like in FPI, to reduce these to an algebraic equation so we need to have the differentiability of wavelets. As was mentioned earlier, Daubechies wavelet of order 2 would have infinite number of discontinuities in derivative so we cannot use it for our purpose. $D6$ (order 3) is barely differentiable¹⁴ but we would like a little more “smoothness” for the numerical stability of the integration. We are at the same time limited by the fact that the higher the order, the more demanding our computation becomes. Hence, we restrict ourselves even further for our choice of wavelets to Daubechies wavelets of order 6 to 10.

One of the tricks one can use to expediate the computation in FPI is to tabulate the Fourier terms beforehand. This means that once the decision on how many Fourier terms would be used is made, one can call on the internal sine function to store the values at each grid point in memory and use these numbers to construct the paths as one samples around the coefficients. This can be done because the paths are just the linear combinations of sine terms and will reduce the number of function calls enormously. One can employ the same technique in WPIMC; however, we choose to use inverse FWT to calculate the paths from the sampled wavelet coefficients each time of the sampling and reduce the memory usage instead.

The number of sampling points for FWT is directly related to how fine a scale one can examine. It also influences the stability of the numerical integration. In most cases, 1024 points, which correspond to index $j=9$, are enough. The numerical integration could make use of some sophisticated quadratures suitable for wavelets;¹⁵ however, we choose to employ the standard trapezoidal rule to keep the algorithm simple.

V. CALCULATIONS

As an illustration of WPIMC, we perform calculations with model potentials. WPIMC calculations are compared to (primitive) FPI results and also Numerical Matrix Multiplication (NMM)¹⁶ or analytic results where applicable.

The first problem we attempt to solve is the Lennard-Jones (LJ) cage potential. The potential is described by

$$V(x) = 4\epsilon \left[\left(\frac{\sigma}{a-x} \right)^{12} - \left(\frac{\sigma}{a-x} \right)^6 + \left(\frac{\sigma}{a+x} \right)^{12} - \left(\frac{\sigma}{a+x} \right)^6 \right]. \quad (13)$$

FIG. 2. Plot of potential energy average as a function of the number of expansion terms.

This model potential can approximate a molecule in a bed of identical molecules. We set $\epsilon = 1.083114 \times 10^{-4}$ eV, $\sigma = 5.595463$ Å, and $a = 6.714556$ Å to match the parameters appropriate for molecular hydrogen.¹⁷ For this particular example, we use two different wavelets for our WPIMC implementation— $D12$ and $D20$.

We solve the LJ cage potential problem with increasing number of wavelet terms and compare the result with FPI calculation in Fig. 2. In this case and all of the following calculations, we use for comparison, “primitive” FPI,⁵ so designated to distinguish the method from *partial averaging* FPI and other related approaches. The run times for WPIMC and FPI are of the same order being approximately 35 000 seconds (WPIMC: $D12$) and 7200 seconds (FPI) for eight million Monte Carlo points on a single R10000 processor of SGI Origin 200. FPI performs better because of two reasons. As was mentioned in the preceding section, the FPI program we adopted uses a trick of tabulating the values of sine functions. The fact that in WPIMC, one has to perform numerical differentiations contributes to the better performance of FPI as well.

The dotted constant line is the result calculated with NMM method using 2^{10} Trotter index points, which we regard as “exact” result. We notice that in Fig. 2, the convergence behavior of WPIMC is different from that of FPI. Though there are some bumps along FPI plot, it can be seen that FPI is monotonically decreasing. In comparison, both WPIMC plots are monotonically increasing. We do not yet have an explanation for this difference. It looks as if WPIMC with $D12$ is a better approximation for the earlier part of the calculation. This is probably because $D20$ has larger support and hence takes more terms to completely eliminate the error stemming from wrapped-around-tail effect. Nevertheless, both WPIMC results displays excellent agreement with the value calculated with NMM method.

The one-dimensional particle-in-a-box (PIB) problem is one of the simplest quantum mechanical systems, yet it displays the very nature of quantum effects. Because of the noncontinuous boundary condition imposed on the PIB prob-

FIG. 3. Plot of density matrix element for particle in a box problem at 10 000 K. For both WPIMC and FPI, only the first eight path variables are used in the expansion.

lem, FPI which uses smooth sine functions for the representation of paths, tends to converge slowly with respect to the number of k terms. This is because classical paths for this system, which are most weighted in path integral formulation, are just straight lines bouncing off the infinite walls. In a time-coordinate diagram, these paths have cusps at the boundaries which is not easily represented with sine functions. We take the size of the box to be a unit length, and the mass of particle to be 2, so that the model emulates a hydrogen molecule in a quantum box. The difference in energies between the ground state and the first excited state for this model is about 1282 K.

Since this system can be solved analytically and the density matrix can be obtained exactly, we attempt to calculate the density matrix plot with the initial and final points being at the origin for both FPI and WPIMC. One can calculate the density matrix elements directly by fixing the final point and sampling $V(x)$ with free particle distribution. Alternatively, one can accumulate Monte Carlo points according to Me-

FIG. 5. Plot of density matrix element for particle in a box problem at 100 K. The first eight path variables are used for both WPIMC and FPI.

ropolis acceptance with the Hamiltonian of the system and find the density distribution of the particles using histogram plot up to a scaling constant.

Figures 3–6 show the results. We have used $D12$ since as we saw in the previous example, that the more compact wavelets tend to give better results. All the plots were done with eight terms for both FPI and WPIMC and each of them has 8 million Monte Carlo points accumulated. For the highest temperature (10 000 K), which gives $\beta\Delta E_{n=1} \approx 1$, both FPI and WPIMC give fairly accurate results compared with the exact calculations. However, for low temperatures (100 and 10 K, $\beta\Delta E_{n=2,n=1} \gg 1$), the discrepancies are visible. It seems, though, that WPIMC shows better behavior at the edges. The curves for FPI do not fall off rapidly enough to reflect the quantum fluctuation effect near the edges.

The Helmholtz free energy is defined by the logarithm of the partition function [Eq. (14)],

$$F = -kT \log Q = -\frac{1}{\beta} \log \left(\sum_n e^{-\beta E_n} \right). \quad (14)$$

FIG. 4. Plot of density matrix element for particle in a box problem at 1000 K. The first eight path variables are used for both WPIMC and FPI.

FIG. 6. Plot of density matrix element for particle in a box problem at 10 K. The first eight path variables are used for both WPIMC and FPI.

FIG. 7. Plot of free energy calculation for LJ potential at 10 K as a function of number of coefficients.

The partition function can be obtained by, without explicitly calculating the density matrix elements, taking the ratio of density matrices for a reference system and the system in question

$$\frac{Q}{Q_{\text{ref}}} = \frac{\int dx \langle x | \exp(-\beta H) | x \rangle}{\int dx \langle x | \exp(-\beta H_{\text{ref}}) | x \rangle}. \quad (15)$$

Since the kinetic term is the same for both Hamiltonians, we can write $H = H_{\text{ref}} + V - V_{\text{ref}}$. Then Eq. (15) can be written as

$$\begin{aligned} \frac{Q}{Q_{\text{ref}}} &= \frac{\int dx \langle x | \exp(-\beta H_{\text{ref}}) | x \rangle \langle x | \exp(-\beta(V - V_{\text{ref}})) | x \rangle}{\int dx \langle x | \exp(-\beta H_{\text{ref}}) | x \rangle} \\ &= \frac{\int dx d\vec{w} \exp(-S_{\text{ref}}(x, x, \vec{w})) \exp(-\beta(V - V_{\text{ref}}))}{\int dx d\vec{w} \exp(-S_{\text{ref}}(x, x, \vec{w}))} \end{aligned} \quad (16)$$

using the usual definition of S from Ref. 5.

We can determine the Helmholtz free energy from Eq. (11) by taking the free particle as a reference. With the free particle reference, Eq. (11) is evaluated by computing the potential energy difference with Monte Carlo points generated from the reference action.

For this problem we again turn to the LJ cage potential and use particle-in-a-box as a reference system. The reference to PIB system has a couple of merits. First of all, since the LJ cage potential has singularities at $x = \pm a$, numerical instabilities can occur near those points. One can circumvent this problem by restricting the range of motion for the particle to be within these points. We do that by setting the size of the box to be smaller than a . Second, PIB is another system for which we know the analytic solution of the partition function. We set the temperature to 10 K and the rest of the parameters the same as in the earlier example of the Lennard-Jones potential problem. We generate random paths using Metropolis procedure with the free particle action that is bound by $x = \pm 6$ and sample the exponential of LJ cage potential.

Figure 7 shows the convergence of both FPI and WPIMC results with respect to the number of expansion coefficients. Again, the dotted constant line indicates the value

calculated with NMM method. FPI and WPIMC show comparable convergence behavior in this case. The monotonicity for both methods is the same as well, as opposed to the potential energy average case. This might have to do with the fact that there are two potentials involved in these estimates.

VI. CONCLUSION

After presenting a brief description of different path integral Monte Carlo methods and relevant portion of wavelet theory, we have established a wavelet formulation of path integral Monte Carlo method. This formulation was accomplished by using a particular family of wavelets, namely Daubechies compactly supported wavelets. In actual implementation of these wavelets, readily available fast wavelet transform routines, which are based on the idea of filters, were adopted. In an analogue to Fourier path integral Monte Carlo, paths are represented by linear combination of wavelets with straight lines between two points in time-coordinate space. The difference between FPI and WPIMC lies in the fact that for WPIMC, kinetic term must be integrated numerically. This condition also puts restriction on the choice of wavelet families to be used in the implementation of WPIMC. Although the support of Daubechies wavelets is compact, for the first few terms of higher order families there are tails spilling over the unit interval in which we are working. To correct this, we put an extra linear term in the expression for the paths with wavelet expansion to force the boundary condition. This correction poses no convergence problem either mathematically or numerically.

Just as in FPI, in implementing WPIMC, one has to truncate the number of terms in the expansion in actual computation. It is expected from examples of engineering applications, that wavelets should be able to describe paths in this space for some potentials better than Fourier terms. This means that with fewer terms, wavelet expansion can describe a typical path for some potentials than Fourier expansion.

In the case of the Lennard-Jones cage potential, WPIMC seems to exhibit better convergence with respect to the number of expansion terms than FPI. In addition to the Lennard-Jones cage potential, particle-in-a-box and free energy estimate for the LJ cage potential were used to test WPIMC. For the PIB problem, we calculate the diagonal density matrix elements by plotting the distribution of Monte Carlo points. It is speculated that, from the result of the PIB problem, WPIMC shows better behavior in a pathological case like "infinite wall." Wavelets are usually superior to Fourier series in describing "cuspy" functions and a classical path in PIB problem would have cusps at the boundaries. It must be mentioned, however, that improved FPI methods such as partial averaging method give better results than the "primitive" FPI used here as a comparison although direct comparison between these methods and WPIMC has not been done. Free energy estimates for the LJ cage potential problem turned out to be similar for FPI and WPIMC.

It should be noted that there is a difference between the usage of wavelets in WPIMC and that of other electronic structure calculations.⁸⁻¹⁰ Previous applications of wavelets in electronic structure calculation were to represent wave functions. Certainly, for bound states with high barriers,

wavelets have clear advantage over plane waves in describing the wave functions because wavelets can catch localized behavior of functions much better. However, in our case of WPIMC, paths in time-coordinate diagrams are not radically different for potentials with highly localized behavior. In that regard, the usual advantage of wavelets is not well pronounced for WPIMC. Nevertheless, WPIMC does show similar behavior to FPI even for the rather “benign” potentials such as LJ cage. It remains to be seen if there exists a class of problems in which WPIMC is much more efficient than FPI or other PIMC methods. This certainly calls for further investigation on the subject.

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