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An Adaptive, Kink-based Approach to Path Integral Calculations

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Abstract

A kink-based expression for the canonical partition function is developed using Feynman's path integral formulation of quantum mechanics and a discrete basis set. The approach is exact for a complete set of states. The method is tested on the 3x3 Hubbard model and overcomes the sign problem seen in traditional path integral studies of fermion systems. Kinks correspond to transitions between different N-electron states, much in the same manner as occurs in configuration interaction calculations in standard *ab initio* methods. The different N-electron states are updated, based on which states occur frequently during a Monte Carlo simulation, giving better estimates of the true eigenstates of the Hamiltonian.

I. Introduction

Studies of disordered and/or finite size electronic systems, such as clusters, amorphous solids, or quantum dots pose challenges for computational methods. The difficulties include the need to accurately treat electron-electron correlation and to include finite temperature effects (particularly as they affect the atomic positions.) The present work is motivated by the desire to simulate large, multi-electron clusters. Studies of these systems are hindered by the need to identify and/or explore global and local minima. The rapid growth in the number of minima with cluster size makes the development of precise, accurate and fast computational algorithms essential for the study of large systems. Often, isomers have similar energies, which requires both the calculation of free energies and the accurate inclusion of electron-electron correlation in order to have a viable method. Feynman's path integral (PI) formulation of quantum mechanics has the potential to provide such a method and is the focus of this work, as its features include exact inclusion of correlation and the calculation of the partition function, which allows both the correct sampling of different geometries and the simultaneous treatment of electronic and geometric degrees of freedom. The latter is a major advantage, as it does not require an accurate estimate of the electronic energy at each set of atomic coordinates. To see this, we can write the partition function for a system with electronic and geometric degrees of freedom as

$$Q \;=\; \int d\mathbf{R}^N \sum_{\{\alpha\}} \rho(\mathbf{R}^N, \{\alpha\}, \beta) \tag{1}$$

where $\mathbf{R}^N$ denotes the set of geometric coordinates, $\{\alpha\}$ denotes the electronic basis set, and ρ is the canonical partition function at an inverse temperature β. If this is evaluated by sampling $\{\mathbf{R}^N\}$ and $\{\alpha\}$ from $|\rho|$, we see that new geometries can be sampled without having a converged electronic state ($\{\alpha\}$ does not need to correspond to the ground or excited state). Effectively, the electronic and geometric optimizations can be carried out *simultaneously*, in contrast to conventional electronic optimization methods, in which a converged energy or set of forces is necessary when changing geometries. The result is that, in principle, the sampling of geometric phase space can be accomplished in a time on the order of the time required for a single electronic energy calculation.

Most path integral approaches use a complete set of states, namely, the position representation, which offers a route to an "exact" determination of the partition function for a many-body system.[1,2,3,4,5,6,7,8,9,10,11,12,13,14,15,16,17,18] These approaches have been frustrated by the sign of the fermion density matrix, which can be positive or negative and can lead to computational difficulties in obtaining precise results. Thus, before the PI method can be applied to the study of clusters and other multiple-minima systems, it is necessary to develop ways to avoid the sign problem. The sign problem is independent of whether or not the atomic positions are fixed. Hence, in this first paper on the subject, we focus on electronic degrees of freedom with fixed atomic positions and leave the extension to varying atomic positions to future work. We note in passing, though, that many interesting systems have fixed atomic positions (e.g., quantum dots[19]), so that the developments in this paper can have immediate applications.

Herein, we abandon the use of the position representation and use a finite basis set in order to avoid some of the difficulty inherent with the position representation. It is well known that finite basis sets (for example, Gaussian basis sets) are capable of producing accurate results for many systems.[20] We use finite basis sets and the discretized version of the path integral expression for Q, the canonical partition function, to develop a "kink" expansion[21,22] for Q. In the discretized version of Q, paths are divided into small imaginary time segments. When using finite basis sets a path will spend some imaginary time in one (many-electron) state (this time may involve several imaginary time segments), have a transition to another state during one imaginary time segment, spend some imaginary time in the second state, have a transition, etc. The transitions between states are called "kinks".[22] A path can therefore be classified by the number of kinks and states involved. When we rewrite the expression for Q in terms of kinks and states, we call this a kink expansion. We note that kinks can correspond to excitations from the ground (Hartree-Fock) state analogous to those seen in configuration interaction (CI) calculations. The expression we develop will give the exact value of Q (including electron-electron correlation) for a complete set of states. The zero kink contribution to Q will have no sign problems, since the system is in a single state. With a properly chosen ground state, it is possible that convergence of the path integral can be obtained with just a few kinks; this would significantly reduce the sign problem, thereby increasing the speed and precision of a calculation. A good choice for the ground state can be obtained

using a Monte Carlo simulation, in which the different N-electron states that appear during the simulation are used to update the estimates of the ground and excited states in a way that includes electron-electron correlation. We call this approach an adaptive approach, since the Monte Carlo algorithm allows the estimates for the ground and excited state wavefunctions to evolve according to the statistical sampling of the different N-electron states.

In the following, we develop a closed form expression for the canonical partition function, cast as a kink expansion. We apply our formulation to a model problem, the 2-D Hubbard model and demonstrate the efficacy of the approach.

II.   Kink Formalism

The kink formalism described here assumes a set (usually finite) of orthonormal, N-particle states, which we denote by $\{\alpha_i\}$. In terms of these states, the partition function can be written

$$Q = Tr\left\{e^{-\beta H}\right\} = \sum_j \left\langle \alpha_j | e^{-\beta H} | \alpha_j \right\rangle \tag{2}$$

We write this as

$$
\begin{aligned}
Q &= \lim_{P \to \infty} Q\left(P\right) \\
Q\left(P\right) &= \sum_{j_1, j_2, \ldots, j_P} \left\langle \alpha_{j_1} | \exp(-\frac{\beta}{P}H) | \alpha_{j_2} \right\rangle \left\langle \alpha_{j_2} | \exp(-\frac{\beta}{P}H) | \alpha_{j_3} \right\rangle \cdots \\
&\qquad \left\langle \alpha_{j_P} | \exp(-\frac{\beta}{P}H) | \alpha_{j_1} \right\rangle
\end{aligned}
\tag{3}
$$

The introduction of P allows high temperature approximations for the matrix elements. In this form, the sign problem can be easily seen. Since each of the matrix elements in Eqn 3 can be positive, negative, or zero, the sign of the summand can be negative for some sets of $\{\alpha_j\}$. Thus, during a Monte Carlo simulation, the estimator for Q can change sign, leading to large statistical errors. This alternation of sign is the source of difficulties in using the path integral formulation to study multi-fermion systems. We focus on an expression for $Q\left(P\right)$. The kink expansion is obtained by recasting the sum over $\{\alpha_j\}$ as a sum with all j_k equal (no kinks), one j_k different (2 kinks), two j_k different (3 kinks), etc:

$$Q\left(P\right) = \sum_{j_1}\left[\left\langle\alpha_{j_1}|\exp(-\frac{\beta}{P}H)|\alpha_{j_1}\right\rangle\right]^{P} +$$

$$\sum_{j_1,j_2}\sum_{n=0}^{P-2}\left[\left\langle\alpha_{j_1}|\exp(-\frac{\beta}{P}H)|\alpha_{j_1}\right\rangle\right]^{n}\left[\left\langle\alpha_{j_2}|\exp(-\frac{\beta}{P}H)|\alpha_{j_2}\right\rangle\right]^{P-2-n} \times$$

$$\left[\left\langle\alpha_{j_1}|\exp(-\frac{\beta}{P}H)|\alpha_{j_2}\right\rangle\right]^{2} + \cdots \tag{4}$$

where the first term is the zero kink term and the second the two kink term. In this and the following equations, $j_1 \neq j_2, j_2 \neq j_3$, etc. If we set

$$\epsilon = \beta/P \tag{5}$$

,

$$x_j = \langle\alpha_j|\exp(-\epsilon H)|\alpha_j\rangle \tag{6}$$

and

$$t_{ij} = \langle\alpha_i|\exp(-\epsilon H)|\alpha_j\rangle \tag{7}$$

we can write the expression for $Q\left(P\right)$:

$$Q\left(P\right) = \sum_{j}x_j^{P} + \sum_{n=2}^{P}\left(\prod_{i=1}^{n}\sum_{j_i}\right)\left(\prod_{k=1}^{n}t_{j_k,j_{k+1}}\right)\left(\prod_{k=1}^{n}\sum_{l_k=0}^{P-n}\right)\left(\prod_{k=1}^{n}x_{j_k}^{l_k}\right)\delta_{l_1+l_2+\cdots+l_n,P-n} \tag{8}$$

where the first term is the zero kink term and $j_{P+1} \equiv j_1$. Recognizing that there are $\binom{P}{n}$ ways to put the n kinks at the different P sites, we can choose the location of the first kink and rewrite our expression as

$$Q\left(P\right) = \sum_{j}x_j^{P} +$$

$$\sum_{n=2}^{P}\frac{P}{n}\left(\prod_{i=1}^{n}\sum_{j_i}\right)\left(\prod_{k=1}^{n}t_{j_k,j_{k+1}}\right) \times$$

$$\sum_{l_n=0}^{P-n}\sum_{l_{n-1}=0}^{P-n-l_n}\cdots\sum_{l_2=0}^{P-n-l_n-l_{n-1}-\cdots l_3}x_{j_n}^{l_n}x_{j_{n-1}}^{l_{n-1}}\cdots x_{j_2}^{l_2}x_{j_1}^{P-n-l_n-l_{n-1}-\cdots-l_2} \tag{9}$$

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With the shorthand notation $S_j \equiv l_n + l_{n-1} + \cdots + l_j$, we have

$$
\begin{aligned}
Q(P) \;=\; & \sum_j x_j^P + \\
& \sum_{n=2}^{P} \frac{P}{n} \left(\prod_{i=1}^{n} \sum_{j_i} \right) \left(\prod_{k=1}^{n} t_{j_k, j_{k+1}} \right) \times \\
& \sum_{l_n=0}^{P-n} \sum_{l_{n-1}=0}^{P-n-S_n} \cdots \sum_{l_2=0}^{P-n-S_3} x_{j_n}^{l_n} x_{j_{n-1}}^{l_{n-1}} \cdots x_{j_2}^{l_2} x_{j_1}^{P-n-S_2}
\end{aligned}
\tag{10}
$$

Consider the term

$$
Q_n = \frac{P}{n} \left(\prod_{i=1}^{n} \sum_{j_i} \right) \left(\prod_{k=1}^{n} t_{j_k, j_{k+1}} \right) \sum_{l_n=0}^{P-n} \sum_{l_{n-1}=0}^{P-n-S_n} \cdots \sum_{l_2=0}^{P-n-S_3} x_{j_n}^{l_n} x_{j_{n-1}}^{l_{n-1}} \cdots x_{j_2}^{l_2} x_{j_1}^{P-n-S_2}
\tag{11}
$$

We first assume that $x_{j_1} \neq x_{j_2} \neq \cdots \neq x_{j_n}$ and define

$$
S(\{x_j\}, n) = \sum_{l_n=0}^{P-n} \cdots \sum_{l_2=0}^{P-n-S_3} x_{j_n}^{l_n} x_{j_{n-1}}^{l_{n-1}} \cdots x_{j_2}^{l_2} x_{j_1}^{P-n-S_2}
\tag{12}
$$

Using,

$$
\sum_{l=0}^{M} \left(\frac{x_i}{x_1} \right)^l = \frac{1 - \left(\frac{x_i}{x_1} \right)^{M+1}}{1 - \left(\frac{x_i}{x_1} \right)}
\tag{13}
$$

we find

$$
\begin{aligned}
\sum_{l_2=0}^{P-n-S_3} x_{j_2}^{l_2} x_{j_1}^{P-n-S_2} \;=\; & \sum_{l_2=0}^{P-n-S_3} \left(\frac{x_{j_2}}{x_{j_1}} \right)^{l_2} x_{j_1}^{P-n-S_3} \\
=\; & x_{j_1}^{P-n-S_3} \left(\frac{1 - \left(\frac{x_{j_2}}{x_{j_1}} \right)^{P-n-S_3+1}}{1 - \left(\frac{x_{j_2}}{x_{j_1}} \right)} \right) \\
=\; & \frac{x_{j_1}^{P-n-S_3+1} - x_{j_2}^{P-n-S_3+1}}{x_{j_1} - x_{j_2}} \\
=\; & \sum_{k=1}^{2} \frac{x_{j_k}^{P-n-S_3+1}}{\prod_{m \neq k}^{2} (x_{j_k} - x_{j_m})} \\
\equiv\; & S(\{x_j\}, 2, n)
\end{aligned}
\tag{14}
$$

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We now proceed by induction to develop a general form for $S\left(\{x_j\}, n\right)$. Assume that

$$S\left(\{x_j\}, i-1, n\right) = \sum_{k=1}^{i-1} \frac{x_{j_k}^{P-n-S_i+(i-2)}}{\prod\limits_{k \neq m}^{i-1}\left(x_{j_k} - x_{j_m}\right)}$$

Consider the next summation in Eq. 12:

$$S\left(\{x_j\}, i, n\right) \sum_{l_i=0}^{P-n-S_{i+1}} x_{j_i}^{l_i} \sum_{k=1}^{i-1} \frac{x_{j_k}^{P-n-S_i+(i-2)}}{\prod\limits_{k \neq m}^{i-1}\left(x_{j_k} - x_{j_m}\right)}$$

$$= \sum_{l_i=0}^{P-n-S_{i+1}} x_{j_i}^{l_i} S\left(\{x_j\}, i-1, n\right)$$

$$= \sum_{l_i=0}^{P-n-S_{i+1}} x_{j_i}^{l_i} \sum_{k=1}^{i-1} \frac{x_{j_k}^{P-n-S_{i+1}-l_i+(i-2)}}{\prod\limits_{k \neq m}^{i-1}\left(x_{j_k} - x_{j_m}\right)}$$

$$= \sum_{k=1}^{i-1} \frac{x_{j_k}^{P-n-S_{i+1}+(i-2)}}{\prod\limits_{k \neq m}^{i-1}\left(x_{j_k} - x_{j_m}\right)} \times \frac{1-\left(\frac{x_{j_i}}{x_{j_k}}\right)^{P-n-S_{i+1}+1}}{1-\left(\frac{x_{j_i}}{x_{j_k}}\right)}$$

$$= \sum_{k=1}^{i-1} \frac{x_{j_k}^{P-n-S_{i+1}+(i-1)}}{\prod\limits_{k \neq m}^{i}\left(x_{j_k} - x_{j_m}\right)} - \sum_{k=1}^{i-1} \frac{x_{j_k}^{i-2} x_{j_i}^{P-n-S_{i+1}+1}}{\left(x_{j_k} - x_{j_i}\right)\prod\limits_{k \neq m}^{i-1}\left(x_{j_k} - x_{j_m}\right)} \qquad (15)$$

Now

$$-\sum_{k=1}^{i-1} \frac{x_{j_k}^{i-2} x_{j_i}^{P-n-S_{i+1}+1}}{\left(x_{j_k} - x_{j_i}\right)\prod\limits_{m \neq k}^{i-1}\left(x_{j_k} - x_{j_m}\right)}$$

$$= \frac{x_{j_i}^{P-n-S_{i+1}+(i-1)}}{\prod\limits_{k \neq i}^{i}\left(x_{j_i} - x_{j_k}\right)} \times \sum_{k=1}^{i-1} \frac{\left(\frac{x_{j_k}}{x_{j_i}}\right)^{i-2} \prod\limits_{m \neq i}^{i}\left(x_{j_i} - x_{j_m}\right)}{\left(x_{j_i} - x_{j_k}\right)\prod\limits_{m \neq k}^{i-1}\left(x_{j_k} - x_{j_m}\right)}$$

$$= \frac{x_{j_i}^{P-n-S_{i+1}+(i-1)}}{\prod\limits_{k \neq i}^{i}\left(x_{j_i} - x_{j_k}\right)} \times \sum_{k=1}^{i-1} \frac{\left(\frac{x_{j_k}}{x_{j_i}}\right)^{i-2} \prod\limits_{m \neq k}^{i-1}\left(x_{j_i} - x_{j_m}\right)}{\prod\limits_{m \neq k}^{i-1}\left(x_{j_k} - x_{j_m}\right)}$$

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$$= \frac{x_{j_i}^{P-n-S_{i+1}+(i-1)}}{\prod\limits_{k\neq i}^{i}\left(x_{j_i}-x_{j_k}\right)} \times \frac{1}{x_{j_i}^{i-2}}\sum\limits_{k=1}^{i-1}\frac{\prod\limits_{m\neq k}^{i-1}\left(x_{j_i}-x_{j_m}\right)}{\prod\limits_{m\neq k}^{i-1}\left(1-\frac{x_{j_m}}{x_{j_k}}\right)} \tag{16}$$

Notice that

$$\sum\limits_{k=1}^{i-1}\frac{\prod\limits_{m\neq k}^{i-1}\left(x_{j_i}-x_{j_m}\right)}{\prod\limits_{m\neq k}^{i-1}\left(1-\frac{x_{j_m}}{x_{j_k}}\right)} \equiv \sum\limits_{k=1}^{i-1}l_k(x_{j_i}) \tag{17}$$

is an i-2 order polynomial in x_{j_i}. Consider $y(x) = \sum\limits_{k=1}^{i-1}l_k(x)$. This is an i-2 order polynomial in x. Since $l_k(x_{j_l}) = x_{j_l}^{i-2}\delta_{k,l}$, $y(x)$ is an i-2 order polynomial that has the value $x_{j_k}^{i-2}$ at the i-1 points $x_{j_1}, x_{j_2}, \ldots, x_{j_{i-1}}$. Since $y(x)$ is an i-2 order polynomial, we must have $\sum\limits_{k=1}^{i-1}l_k(x) = x^{i-2}$. Therefore,

$$\frac{1}{x_{j_i}^{i-2}}\sum\limits_{k=1}^{i-1}\frac{\prod\limits_{m\neq k}^{i-1}\left(x_{j_i}-x_{j_m}\right)}{\prod\limits_{m\neq k}^{i-1}\left(1-\frac{x_{j_m}}{x_{j_k}}\right)} = 1 \tag{18}$$

and

$$\begin{aligned}
&\sum\limits_{k=1}^{i-1}\frac{x_{j_k}^{P-n-S_{i+1}+(i-1)}}{\prod\limits_{k\neq m}^{i}\left(x_{j_k}-x_{j_m}\right)} - \sum\limits_{k=1}^{i-1}\frac{x_{j_k}^{i-2}x_{j_i}^{P-n-S_{i+1}+1}}{\left(x_{j_k}-x_{j_i}\right)\prod\limits_{k\neq m}^{i-1}\left(x_{j_k}-x_{j_m}\right)}\\
&= \sum\limits_{k=1}^{i}\frac{x_{j_k}^{P-n-S_{i+1}+(i-1)}}{\prod\limits_{k\neq m}^{i}\left(x_{j_k}-x_{j_m}\right)}\\
&= S\left(\{x_j\}, i, n\right)
\end{aligned} \tag{19}$$

Therefore, by induction, we can show that

$$S\left(\{x_j\}, n\right) = \sum\limits_{k=1}^{n}\frac{x_{j_k}^{P-1}}{\prod\limits_{k\neq m}^{n}\left(x_{j_k}-x_{j_m}\right)} \tag{20}$$

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Next consider the case where some of the x_{j_k} are equal. The general result can be inferred by assuming x_0 occurs twice in the sum:

$$\cdots \sum_{k=0}^{P-m} x_0^k \sum_{l_1=0}^{P-m-k} x_1^{l_1} \sum_{l_2=0}^{P-m-k-S_1} x_2^{l_2} \cdots \sum_{l_n=0}^{P-m-k-S_{n-1}} x_n^{l_n} \sum_{j=0}^{P-m-k-S_n} x_0^j \sum_{i=0}^{P-m-k-S_n-j} x_i^i \cdots \tag{21}$$

Now

$$\sum_{l=0}^{M} x_l^l \sum_{k=0}^{M-l} x_0^k = \sum_{k=0}^{M} x_0^k \sum_{l=0}^{M-k} x_l^l \tag{22}$$

so Eq. 21 becomes

$$\cdots \sum_{k=0}^{P-m} x_0^k \sum_{j=0}^{P-m-k} x_0^j \sum_{l_1=0}^{P-m-k-j} x_1^{l_1} \cdots \tag{23}$$

As a result, if there are s identical x_0, we will arrive at

$$\cdots \sum_{k_1=0}^{P-m} \sum_{k_2=0}^{P-m-S_1} \sum_{k_3=0}^{P-m-S_2} \cdots \sum_{k_s=0}^{P-m-S_{k_s-1}} x_0^{k_1+k_2+\cdots+k_s} \sum_{l=0}^{P-m-S_{k_s}} x_l^l \cdots \tag{24}$$

$$= \cdots \sum_{k_1=0}^{P-m} \sum_{k_2=0}^{P-m-S_1} \sum_{k_3=0}^{P-m-S_2} \cdots \sum_{k_{s-1}=0}^{P-m-S_{k_s-2}} \sum_{k_s=S_{k_s-1}}^{P-m} x_0^{k_s} \sum_{l=0}^{P-m-k_s} x_l^l \cdots$$

$$= \cdots \sum_{k_s=0}^{P-m} x_0^{k_s} \sum_{k_1=0}^{k_s} \sum_{k_2=0}^{k_s-S_1} \cdots \sum_{k_{s-1}=0}^{k_s-S_{k_s-2}} \sum_{l=0}^{P-m-k_s} x_l^l \cdots$$

where we used $\sum_{k=o}^{M-N} \sum_{j=k+N}^{M} = \sum_{j=N}^{M} \sum_{k=0}^{j-N}$. Let

$$W(s, k_s) \equiv \sum_{k_1=0}^{k_s} \sum_{k_2=0}^{k_s-S_1} \cdots \sum_{k_{s-1}=0}^{k_s-S_{k_s-2}} \tag{25}$$

Now we assert that $W(s, k_s) = \binom{k_s+s-1}{s-1}$. When $s = 2$, $W(s, k_s) = k_s + 1 = \binom{k_s+s-1}{s-1}$. To show this in general, we use proof by induction. If $W(s-1, k_s - k_1) = \binom{k_s-k_1+s-2}{s-2}$, then

$$W(s, k_s) = \sum_{k_1=0}^{k_s} \binom{k_s - k_1 + s - 2}{s - 2}$$

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$$
= \sum_{k_1=0}^{k_s} \frac{(k_s + s - 2 - k_1)!}{(s-2)! \, (k_s - k_1)!}
$$

$$
= \sum_{k_1=-k_s}^{0} \frac{(s - 2 - k_1)!}{(s-2)! \, (-k_1)!}
$$

$$
= \sum_{k_1=0}^{k_s} \frac{(s - 2 + k_1)!}{(s-2)! \, (k_1)!}
$$

$$
= \sum_{k_1=0}^{k_s} \binom{s - 2 + k_1}{s - 2}
$$

$$
= \binom{s - 1 + k_s}{s - 1} \tag{26}
$$

where the last identity is taken from Gradshteyn and Ryzhik.[23] Thus, Eqn. 24 becomes

$$
\cdots \sum_{k_s=0}^{P-m} \binom{k_s + s - 1}{s - 1} x_0^{k_s} \sum_{l=0}^{P-m-k_s} x_l^{l} \cdots
$$

$$
= \cdots \frac{1}{(s-1)!} \sum_{k_s=0}^{P-m} \frac{d^{s-1}}{dx_0^{s-1}} x_0^{k_s+s-1} \sum_{l=0}^{P-m-k_s} x_l^{l} \cdots \tag{27}
$$

Thus, we have for m **distinct** x_{j_k}'s, each occurring s_{j_k} times

$$
S\left(\{x_j\}, n, m, \{s_j\}\right) = \prod_{k=1}^{m} \left[\frac{1}{(s_{j_k}-1)!} \frac{d^{s_{j_k}-1}}{dx_{j_k}^{s_{j_k}-1}} x_{j_k}^{s_{j_k}-1} \right] \sum_{l=1}^{m} \frac{x_{j_l}^{P-n+m-1}}{\prod_{i \neq l}(x_{j_l} - x_{j_i})} \tag{28}
$$

The derivatives can be evaluated recursively and therefore we have a final expression for Q:

$$
Q\left(P\right) = \sum_{j} x_j^{P} +
$$

$$
\sum_{n=2}^{P} \frac{P}{n} \left(\prod_{i=1}^{n} \sum_{j_i} \right) \left(\prod_{k=1}^{n} t_{j_k, j_{k+1}} \right) S\left(\{x_j\}, n, m, \{s_j\}\right) \tag{29}
$$

This expression can be evaluated using a Monte Carlo algorithm in which both N-electron states and kinks are sampled. While the number of kinks

can grow to be P, in practical calculations it is plausible that a good choice of states will require only a limited number of kinks. If there are 0 or 2 kinks, it is clear that the Monte Carlo estimator will be positive; for more than 2 kinks, there will be some negative values for the estimator. However, as the estimate for the ground and excited states improves, the sign problems will be reduced.

III.   Application: 2-D Hubbard Model

The formalism was applied to the 2-D Hubbard model.[24] In this model, the Hamiltonian is given by

$$\mathcal{H} = at + bU \tag{30}$$

where t is a hopping term that allows hopping between nearest neighbor sites and U is an repulsive energy term that has non-zero contributions when two particles are on the same site. In this work, we chose a 3x3 lattice, $a = -1.0$, $b = 4.0$, and periodic boundary conditions were *not used*. We applied the kink formalism to several occupancies of the lattice: $N_{electron} = 3$, 4, and 5. The number of up- and down-spin electrons is given in Table 1. Temperature was chosen to represent "typical" temperatures encountered in studies of clusters: $\beta\Delta E > 10$ where ΔE is the difference in energy between the ground and first excited state. This value was chosen assuming a 0.1-1 eV gap between ground and excited states (a typical value in small metallic clusters) and a temperatures on the order of a hundred Kelvin). The values of β are given in Table 1.

The method was made adaptive in the following manner. An initial set of N-electron states was chosen by diagonalizing the single particle Hamiltonian. We then calculated and stored in memory all the matrix elements $H_{\alpha',\alpha} = \langle \alpha'|H|\alpha \rangle$. These matrix elements can be constructed from:

$$\text{For} \quad |\alpha> \quad = \quad \prod_{i=1}^{N_{electron}} |\alpha_i> \tag{31}$$

$$\left\langle \alpha_i'|t|\alpha_i \right\rangle = \begin{cases} 1 & \alpha_i', \alpha_i \text{ nearest neighbors} \\ 0 & \text{otherwise} \end{cases} \tag{32}$$

$$\left\langle \alpha_1', \alpha_2'|U|\alpha_1, \alpha_2 \right\rangle = \delta_{1,2}\delta_{\alpha_1',\alpha_1}\delta_{\alpha_2',\alpha_2} \tag{33}$$

These were then used to approximate the density matrix elements as:

$$< \alpha' | \exp(-\epsilon H) | \alpha > \quad \approx \quad < \alpha' | (1 - \epsilon H) | \alpha > \qquad (34)$$

P was chosen large enough so that the results were converged to the exact result. For larger basis sets, the storage of matrix elements will not be feasible, but can be calculated "on-the-fly". During the course of the Monte Carlo calculation, we kept track of the N-electron states that appeared at each step. For the first 5000 steps, we periodically performed diagonalizations using only the states that appeared at least 0.1% of the time. Thus, a subset of the total number of N-electron states were diagonalized, using the current set of matrix elements $H_{\alpha',\alpha}$. After each diagonalization, all the Hamiltonian matrix elements were updated. Therefore, after a number of diagonalizations, the states we labeled as α were linear combinations of the original set of N-electron states. During subsequent Monte Carlo steps, we expected the adapted states to produce fewer kinks and to reduce the sign problem.

This adaptive procedure is similar to stochastic diagonalization methods,[25] used to find the lowest eigenvalues of large Hamiltonians. The major difference is that here we include states that couple to excited states in the set of states used for diagonalization (which we must, since we are not focusing solely on obtaining ground state energies, but rather the partition function). Stochastic diagonalization corresponds, roughly, to using the present approach, but limiting the number of kinks to 2 (one of the two states restricted to being the ground state) and performing a diagonalization every time a second kink is accepted. In addition, since the overall goal is to simultaneously sample atomic positions and treat the electronic problem, the Hamiltonian matrix elements we are concerned with will change during the simulation, which is not the case in standard stochastic diagonalization techniques. In an application of the path integral approach to systems other than model systems, it is likely that many of the ideas of stochastic diagonalization can be "borrowed" for use in the adaptive scheme, while at the same time utilizing the power of the path integral method to treat finite temperatures and changing atomic positions. In any event, the adaptive procedure resulted in a new set of correlated N-electron states that were better representations of the eigenstates of the Hamiltonian. After diagonalization, the system was put in the ground state and the number of kinks was set to 0. After 5000 steps, 15000 additional steps with no further diagonalization were taken in order to calculate the total energy.

The results are shown in Table 1. We first rewrote Eqn. 29 as

$$Q(P) = \sum_{n=1}^{P} \left(\prod_{i=1}^{n} \sum_{j_i} \right) \rho_n(\{\alpha_j\}) \qquad (35)$$

Here, $n = 1$ corresponds to the zero kink term and ρ is the density matrix corresponding to n and a specific set of states $\{\alpha\}$ We evaluated the average sign:

$$\langle S \rangle = \frac{\langle \rho_n \rangle}{\langle |\rho_n| \rangle} \qquad (36)$$

For a poorly chosen set of states, $\langle S \rangle$ will be nearly zero.[6] Thus, $\langle S \rangle$ is a good measure of the severity of the sign problem. We also evaluated the average energy via

$$\langle E_{MonteCarlo} \rangle = \frac{\langle -\partial \rho_n / \partial \beta \rangle}{\langle \rho_n \rangle} \qquad (37)$$

by taking the appropriate derivative of Eqn. 29. An examination of Table 1 shows that the average sign of the density matrix is unity and demonstrates that the adaptive approach does indeed overcome the sign problem. An analysis of the number of types of kinks encountered indicated that only 0 and 2 kinks were present after the 5000 step adaptive period. Since the density matrix is always positive for 0 or 2 kinks, this lead to the value of 1.0 for the average sign. Without the adaptive procedure, the average sign would have been very small and the usual sign problems would have been encountered.

It is interesting to examine the convergence of the ground state energy to its final value during the adaptive phase of the simulation (the first 5000 Monte Carlo passes), as well as the number of states involved in the diagonalization. This information is given in Table 2 and Table 3. It is evident that only a subset of the total number of states need to be included at any one diagonalization, which aids in the speed of the calculation. In addition, the energy is seen to converge relatively quickly to a final value during the adaptive stage. $N_{electron} = 3$ and 5 doubly degenerate ground states, leading to 2 states being "visited" a substantial amount of time. Also note that, after the final diagonalization, the ground state energy of $N_{electron} = 4$ is not the exact ground state energy, but the exact average energy is obtained

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during the simulation with the addition of kinks. Finally, we note that the last diagonalization for $N_{electron} = 5$, makes a very small change in the total energy.

It may be noticed that, for each value of $N_{electron}$, a large fraction of the states are involved in one of the diagonalization steps. This leads to the question of whether this is a required feature of the adaptive scheme. To test this, we performed an additional simulation for $N_{electron} = 5$ and restricted the number of states that could be diagonalized at any time to 300. The results are shown in Table 4, from which it is evident that a diagonalization step involving a large fraction of the states is not needed for the adaptive scheme to work, although diagonalizing fewer states at each step does increase the length of the adaptive period.

IV.   Conclusions

The adaptive approach has been shown to be successful in overcoming the sign problem inherent in standard path integral approaches. The use of the closed form expression for the kink expansion allows large values of P to be used. This method needs to be applied to additional systems, to assess its overall utility. In particular, there needs to be an assessment of how the method scales with the number of basis functions. This is not straightforward to determine, since this will depend on what types of schemes are used to speed up the calculation. However, it is likely that, for fixed atomic positions, that the method will scale in time similar to CI calculations, though it will not have to exhaustively evaluate all excitations (singles, doubles, etc.) and may therefore require less time than a traditional CI calculation. In addition, the size of the space of Slater determinants may grow too large for brute force diagonalization, while the adaptive approach can still be used (much in the same way that stochastic diagonalization can be used). Since the electronic calculation can be carried out simultaneously with atomic position optimization, the time for a calculation with varying atomic positions should be comparable to the time required to perform a *single point ab initio* CI calculation. Additionally, as the adaptive wavefunctions become better representations of the exact wavefunction, the calculation should speed up, since only a small number of states will be coupled to the ground state. Future work will assess the applicability of this method to such types of calculations.

V.   Acknowledgments

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Table Captions

Table 1 Caption. Parameters for 3x3 Hubbard Model. $N_{electron}$ is the total number of electron, N_{up} and N_{down} the number of up- and down-spin electrons, respectively, β is the inverse temperature, $< E_{exact} >$ is the exact thermally averaged energy, ΔE is the difference between the ground and first excited states, P is the number of discretization points, $< E_{MonteCarlo} >$ is the average energy from the simulation, and $< S >$ is the average sign of the density matrix. Numbers in parenthesis represent 2 standard deviations.

Table 2 Caption. Number of states included in the diagonalization for the adaptive steps performed during the first 5000 Monte Carlo passes. Diagonalizations were performed after every 500 Monte Carlo passes up to 5000 passes. In addition, diagonalizations were performed after 1 and 100 Monte Carlo steps. The total number of states are 324 (N=3), 1296 (N=4), and 3024 (N=5).

Table 3 Caption. Convergence of the ground state energy with adaptive diagonalizations.

Table 4 Caption. Convergence of the ground state energy with adaptive diagonalization for $N_{electron} = 5$ and with the maximum number of states allowed to be diagonalized restricted to 300. After 5000 passes, diagonalizations were only performed when more than 2 kinks occurred for a significant amount of time. Following the adaptive period, the average energy was calculated and found to be -8.214186 (6).

	$N_{electron} = 3$	$N_{electron} = 4$	$N_{electron} = 5$
N_{up}	2	2	3
N_{down}	1	2	2
β	50.0	200.0	50.0
$< E_{exact} >$	-6.50920068	-7.649675	-8.21418803
$\beta\Delta E$	42.6	46.2	36.0
P	524288	2097152	524288
$< E_{MonteCarlo} >$	-6.50920068(8)	-7.649676(5)	-8.21418801(4)
$< S >$	1.00(0)	1.00(0)	1.00(0)

Table 1:

Table 1 Parameters for 3x3 Hubbard Model. $N_{electron}$ is the total number of electrons, N_{up} and N_{down} the number of up- and down-spin electrons, respectively, β is the inverse temperature, $< E_{exact} >$ is the exact thermally averaged energy, ΔE is the difference between the ground and first excited states, P is the number of discretization points, $< E_{MonteCarlo} >$ is the average energy from the simulation, and $< S >$ is the average sign of the density matrix. Numbers in parenthesis represent 2 standard deviations.

Pass Number	$N_{electron}$=3	$N_{electron}$=4	$N_{electron}$=5
1	1	1	1
100	125	67	310
500	132	453	1404
1000	2	29	1303
1500	2	9	2
2000	2	5	2
2500	2	4	2
3000	2	4	2
3500	2	3	2
4000	2	4	2
4500	2	2	2
5000	2	4	604

Table 2:

Table 2. Number of states included in the diagonalization for the adaptive steps performed during the first 5000 Monte Carlo passes. Diagonalizations were performed after every 500 Monte Carlo passes up to 5000 passes. In addition, diagonalizations were performed after 1 and 100 Monte Carlo steps. The total number of states are 324 (N=3), 1296 (N=4), and 3024 (N=5).

Pass Number	$N_{electron}$=3	$N_{electron}$=4	$N_{electron}$=5
1	-6.13356781	-6.92278137	-7.21199493
100	-6.50883238	-7.55718596	-8.14959112
500	-6.50920068	-7.64950387	-8.21394605
1000	-6.50920068	-7.64958381	-8.21418741
1500	-6.50920068	-7.64962108	-8.21418741
2000	-6.50920068	-7.64963715	-8.21418741
2500	-6.50920068	-7.64964181	-8.21418741
3000	-6.50920068	-7.64964634	-8.21418741
3500	-6.50920068	-7.64964922	-8.21418741
4000	-6.50920068	-7.64965215	-8.21418741
4500	-6.50920068	-7.64965246	-8.21418741
5000	-6.50920068	-7.64965656	-8.21418802

Table 3:

Table 3. Convergence of the ground state energy with adaptive diagonalizations.

Table 4. Convergence of the ground state energy with adaptive diagonalization for $N_{electron} = 5$ and with the maximum number of states allowed to be diagonalized restricted to 300. After 5000 passes, diagonalizations were only performed when more than 2 kinks occurred for a significant amount of time. Following the adaptive period, the average energy was calculated and found to be -8.214186 (6).

Pass Number	States Involved	Energy
1	1	-7.21199493
100	178	-8.12195973
500	295	-8.17901325
1000	257	-8.18986053
1500	274	-8.19522379
2000	275	-8.19876874
2500	227	-8.20054427
3000	283	-8.20333449
3500	283	-8.20517670
4000	245	-8.20888475
4500	236	-8.21053144
5000	213	-8.21132950
5500	294	-8.21260450
6000	300	-8.21349827
6500	293	-8.21396900
7000	289	-8.21407486
7500	6	-8.21407824
8000	3	-8.21407828
8500	284	-8.21412725
9000	202	-8.21414318
9500	3	-8.21414335
10000	4	-8.21414377
12000	221	-8.21415918
12500	231	-8.21417133
14500	199	-8.21417807

Table 4: