Multigrid Solution of a Path Integral Formulation for the Hydrogen Atom†

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1. Introduction

Most methods for Path Integral Monte Carlo (PIMC) simulations are inefficient for paths with large number of points. This is due mostly to the critical slow down (CSD) for lower dimensions and to the volume factor [5] for many dimensions. Furthermore, current applications of PIMC methods for solutions of Schrödinger equations for atomic systems is restricted because of the singularity of the potential functions. These systems are usually solved by Green’s function Monte Carlo (GFMC) algorithms [2-3].

In this work (1) A path integral formulation appropriate for Coulomb potentials is presented is Sec. 2. This formulation is based on a quadratic polynomial approximation of the classical motion. The resulting action integral can be expressed as a standard linear expression of the action integral with an effective potential. This effective potential depends on $\tau^2$, where $\tau$ is the mesh size (time step). (2) A multigrid algorithm using a “unigrid” approach is used for solving the hydrogen atom (Sec. 3). This algorithm uses a linear interpolation of changes to coordinates [5], rather than constant interpolation [1]. The use of linear interpolation eliminates the CSD with simple $V(1,1)$ multigrid cycles. The integrated decorrelation time $\tau_{int}$ is below 10 for all measured observables. In Sec.4 the numerical results with the multigrid algorithm are presented. For comparison, the same problem is solved with a staging algorithm [6-11].

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2. Path integral formulation for the hydrogen atom

In this section, \(r_i, i = 0, \ldots, N - 1\) denotes the 3D coordinate vector \((x_i, y_i, z_i)\) of the electron, \(\tau\) is the meshsize (timestep) of the path and \(N\) is the number of path points. Since only the ground state is considered the path is closed and \(r_N = r_0\). \(V_i\) denotes the potential function at \(r_i\), and \(M\) is the mass of the electron.

The standard first order approximation of the action integral for a path \(\Gamma\) is

\[
S_1(\Gamma) = \tau \sum_{i=0}^{N-1} V_i + \frac{M}{2\tau} \sum_{i=0}^{N-1} (r_{i+1} - r_i)^2.
\]

The relative probability for the path is,

\[P(\Gamma) = e^{-S_1(\Gamma)}.
\]

However, this approximation fails for the Coulomb potential

\[V(r) = -\frac{1}{r}.
\]

The reason is that when the Metropolis [4] algorithm is used to generate new paths, the path points tend to concentrate near \(r = 0\), resulting in meaningless measurements of observables. This happens because near \(r = 0\), the transition probability from large \(r\) is very close to 1. Similarly, since the transition probability from \(r = 0\) to large \(r\) is very small. Hence a path point can not make the transition to larger \(r\), once trapped near \(r = 0\).

In terms of the classical path, the standard approximation (2.1) assumes that during the time \(\tau\), the particle a) Move along the straight line connecting \(r_i\) and \(r_{i+1}\), and b) The time that the particle spends along any portion of that line is proportional to its length. It is mostly the second assumption that breaks down near the singularity, since classically if \(r_i\) is near 0, the particle spends most of its time away from it.

To make a better approximation of the classical motion, assumption a) above is preserved, but instead of b) the motion is assumed to be in a constant force field. For a motion from \(r_i\) to \(r_{i+1}\) the classical acceleration \(a_i\), is given by

\[a_i = -\hat{u}(V(r_{i+1}) - V(r_i))/M|r_{i+1} - r_i|,
\]

where \(\hat{u}\) is the unit vector in the direction from \(r_i\) to \(r_{i+1}\). The position as a function of time is,

\[r(t) = r_i + (r_{i+1} - r_i)((t - t_i)/\tau) + a_i(t - t_i)(t - t_i - \tau).
\]

This classical motion conserves energy. Therefore the total energy \(E_i\) for the motion \(r_i \rightarrow r_{i+1}\) can be taken as the energy at time \(t_i\),

\[E_i = Mv_i^2/2 - 1/r_i,
\]

where \(v_i\) is

\[v_i = (r_{i+1} - r_i)/\tau - a_i\tau.
\]

Thus, the action integral for a path \(\Gamma\) is

\[
S_2(\Gamma) = \tau \sum_{i=0}^{N-1} E_i
\]
2.1 Simplified path integral formulation

From (2.3), the expression for $v_i^2$ contains three terms: 

(i) $(r_{i+1} - r_i)^2/\tau^2$. This is the same expression for the squared velocity that appears in the standard approximation (2.1). 

(ii) $\tau^2a^2$. From (2.2), in the limit $\tau \to 0$, this term for the Coulomb potential is $O(\tau^2/r^4)$. Similarly, in the same limit the term (iii) $-2a_i(r_{i+1} - r_i)$ is $O(1/r^2)$.

Near $r = 0$, the term (ii) is dominant. For large $r$, the standard term (i) is dominant. It is therefore reasonable to approximate the kinetic energy by preserving only terms (i) and (ii), and omitting (iii) altogether. The action integral is then,

$$S(\Gamma) = \left(\frac{M}{2\tau}\right) \sum_{i=0}^{N-1} (r_{i+1} - r_i)^2 - \tau \sum_{i=0}^{N-1} 1/r_i + \tau (A/M) \sum_{i=0}^{N-1} \tau^2/r_i^4,$$  \hspace{1cm} (2.5)

where $A$ is a positive constant. The last two terms can be regarded as a sum over an effective potential

$$\tilde{V}_i(r, \tau) = -1/r_i + A\tau^2/Mr_i^4.$$ \hspace{1cm} (2.6)

Note that the last term in (2.6) acts as a repulsive potential, and thus prevents the path points from falling into $r = 0$. For a fixed $u = A\tau^2/Mr(u)^4$, $r(u)$ decreases as $\sqrt{\tau}$. With $\tilde{V}$ the action integral is

$$S(\Gamma) = \left(\frac{M}{2\tau}\right) \sum_{i=0}^{N-1} (r_{i+1} - r_i)^2 + \tau \sum_{i=0}^{N-1} \tilde{V}_i.$$ \hspace{1cm} (2.7)

This considerably simplifies the Monte Carlo sampling of paths, as its form is the same as the standard approximation (2.1).
3. Multigrid algorithm

To eliminate the correlation between paths, a multigrid algorithm is used for generating paths. The algorithm in this study implements a “unigrid” approach, because of its simplicity. In this approach there is only a single grid and coarse level operations are emulated on this grid. Such an algorithm is not very effective in reducing the volume factor (see [5]) for a large number of dimensions. However, it is effective in eliminating the CSD (see Sec. 4), which is the most important factor in efficiency degradation for lower number of dimensions such as the hydrogen atom. For higher dimensions, a fully multigrided algorithm should be used.

The finest level \( l = 0 \) contains the whole set of points \( i = 0, \ldots, N - 1 \) of the path, corresponding to times \( t_i = i\tau \). \( N \) is assumed to be an integral power of 2. A coarser level \( l = 1, \ldots, l_c \) contains the set of \( n_l = N/2^l \) points \( i_l = n2^l, n = 0, 1, \ldots, n_l \), corresponding to the times \( t_{i_l} = t_{i_l}\tau \).

On the finest level, a relaxation sweep consists of changing the coordinates of each path point in turn, and accepting or rejecting the new position by the standard Metropolis algorithm [4].

To explain the relaxations on coarse grids, the following notation is introduced. Let \( \Gamma_{i_1,i_2} \) be the set of path points corresponding to times \( t_{i_1}, t_{i_1+1}, \ldots, t_{i_2} \). Let \( S_{i_1,i_2} \) be the action integral of \( \Gamma_{i_1,i_2} \):

\[
S_{i_1,i_2} = \left(M/2\tau\right) \sum_{i=i_1}^{i_2-1} (r_{i+1} - r_i)^2 + \tau \sum_{i=i_1}^{i_2} \bar{V}_i,
\]

where \( \bar{V} \) is given by Eq. (2.6).

A relaxation sweep on level \( l > 0 \), is emulated by visiting all path points corresponding to that level. When the point \( i_l \) is visited, simultaneous changes of the coordinates are made to \( \Gamma_{i_l-2^l,i_l+2^l} \). These changes are given by

\[
\bar{\mathbf{d}}_i = \left(1 - \frac{|i_l - i|}{2^l}\right) \bar{\mathbf{\xi}} \delta_l \quad i = i_l - 2^l, \ldots, i_l, \ldots, i_l + 2^l
\]

where \( \delta_l \) is a constant, \( \bar{\mathbf{d}}_i \) is the 3D vector \((\delta_x, \delta_y, \delta_z)\) of changes to the space coordinates \((x, y, z)\) and \( \bar{\mathbf{\xi}} \) is the 3D vector \((\xi_x, \xi_y, \xi_z)\). Each of the components of \( \bar{\mathbf{\xi}} \) is a random variable with uniform distribution in \([-1, 1]\) (See also Sec. 4.1). If \( S^a \) is the action of \( \Gamma_{i_l-2^l,i_l+2^l} \) before changes to coordinates are made, and \( S^b \) is the action after the changes, the new configuration is accepted according to the transition probability

\[
P_{ab} = \min(1, e^{-(S^b-S^a)}).
\]

Paths are generated by cycling on all levels, usually with \( V(1,1) \) cycles. W-cycles or other cycles which increase the number of passes on coarse levels relative to fine levels (i.e. higher cycle indices, [5] works as well, and are effective in reducing the decorrelation times between paths. However, in the “unigrid” approach, the work spent on a coarse level is not
much less than the work on a fine level. Therefore there is not much to gain in efficiency by performing more relaxations on coarse levels. Note, however, that using higher cycle index with the “unigrid” approach is an effective research tool for studying the behavior of the algorithm.

Measurements of observables can be done either on the finest or on coarser levels. Because of the high correlations between adjacent path points on the finest level, some work may be saved making measurements on coarser levels. However, observables that depend on correlations between adjacent path points, such as the mean of squared velocity can not be measured on coarse levels.

4. Numerical experiments

Numerical results for the hydrogen atom with the multigrid algorithm are presented in Sec. 4.1. For comparison, results with a simplified staging algorithm ([9-11]) for the same problem are presented in (Sec. 4.2).

All computations in this section are done with the effective potential (2.6). The results of the calculations are not very sensitive to value of $A$ in (2.6). In all numerical experiments in this section $A = 0.005$ is always used.
4.1 Multigrid results

In Table 1, the results with V(1,1) cycles with the “unigrid” approach (Sec. 3) are described for different number of levels. The meshsize of a level \( l \) with \( N_l \) points is \( \tau_l = 32/N_l \).

In a relaxation sweep on the finest level \((l = 0)\) the \((x_i, y_i, z_i)\) coordinates are changed simultaneously at each path point by adding \( \delta = (\delta_x, \delta_y, \delta_z) \) to the current values. \( \delta \) is calculated by \( \delta = \xi \delta_0 \). \( \delta_0 \) is a constant scalar optimized to yield Metropolis acceptance ratio of \( \sim 0.5 \) on that level. On coarser levels, simultaneous changes are made to the 3 space coordinates of more than one point, as described in Sec.3. As with \( \delta_0 \), the scalar constant \( \delta_l \) for \( l > 0 \) is chosen so that the Metropolis acceptance ratio on that level is \( \sim 0.5 \).

The observables measured are the mean radius of the electron \(< r >\), the mean inverse of the radius \(< 1/r >\) and the mean kinetic energy \(< e_k >\). \(< e_k >\) is approximated by averaging the operator

\[
(M/2\tau^2) ((x_{i+1} - x_i)(x_i - x_{i-1}) + (y_{i+1} - y_i)(y_i - y_{i-1}) + (z_{i+1} - z_i)(z_i - z_{i-1}))
\]

where \( \tau \) is the meshsize ([12]). For each observable the integrated decorrelation time (\( \tau_{int} \)) is listed.

| \( L \) | \( N_0 \)  | \( \tau_0 \) | \( < r > \)  | \( \tau_{int} \) | \( < 1/r > \) | \( \tau_{int} \) | \( < e_k > \) | \( \tau_{int} \) |
|-------|---------|-----------|------------|-------------|-------------|-------------|-------------|-------------|
|  6    |  128    | 0.2500    | 1.431(7)   | 10.0        |  1.130(4)   | 7.0         |  0.80(1)    | 3.0         |
|  7    |  256    | 0.12500   | 1.459(6)   | 7.8         |  1.064(4)   | 6.0         |  0.89(1)    | 2.7         |
|  8    |  512    | 0.062500  | 1.489(7)   | 9.7         |  1.019(3)   | 7.0         |  0.92(1)    | 2.6         |
|  9    | 1024    | 0.031250  | 1.493(4)   | 7.3         |  1.009(2)   | 5.4         |  0.99(1)    | 2.4         |
| 10    | 2048    | 0.015625  | 1.498(3)   | 8.0         |  1.004(3)   | 5.5         |  0.98(1)    | 2.3         |

\( L \) - number of levels
\( N_0 \) - number of points on finest level
\( \tau_0 \) - meshsize of finest level

Table 1 - Multigrid V(1,1) cycles

It is quite evident from the table that for each measured observable no significant CSD exists in the range of 128-2048 path points.

In Table 2 a typical behavior of \( \delta_l \) as a function of \( l \) is described. The results in the table are for the last case listed in Table 1 \((L = 10, N_0 = 2048)\). The Metropolis acceptance ratio (MAR) is listed in the last column. For fine levels, \( \delta_l \) is proportional to the square root of the meshsize. For coarser levels with mean distance between grid points
comparable to $< r >$, $\delta_l$ becomes smaller with increased meshsize.

| $l$ | $\delta_l$ | MAR  |
|-----|-------------|------|
| 0   | 0.125       | 0.505|
| 1   | 0.175       | 0.509|
| 2   | 0.245       | 0.513|
| 3   | 0.343       | 0.516|
| 4   | 0.480       | 0.518|
| 5   | 0.672       | 0.511|
| 6   | 0.941       | 0.479|
| 7   | 1.054       | 0.487|
| 8   | 0.922       | 0.490|
| 9   | 0.646       | 0.515|

Table 2 - behavior of $\delta_l$
4.2 Staging algorithm results

As a comparison with the performance of the multigrid algorithm the results of a staging algorithm for the same problem are described. This staging algorithm is similar to the algorithm used in [6], [7], and is a simplified version of the algorithm described in [8].

In a relaxation sweep, each point \( i \) of the path becomes an end point of a chain of adjacent \( p \) path points \( i, i+1, \ldots, i+p+1 \). The two end points \( i \) and \( i+p+1 \) are held fixed and the coordinates of all the other chain points are changed simultaneously with means and variances of a Levy walk. The new chain configuration is then accepted or rejected. Few trials per chain may be repeated to increase efficiency.

Table 3 describes the results of the staging algorithm for the hydrogen atom, with different number of path points \( (N) \), chain length \( (N_c, \text{ including the end points}) \) and trials per chain \( (N_{\text{try}}) \). The meshsize \( \tau \) is \( 32/N \). The last three columns lists 1) the computational work per relaxation sweep \( (W_r) \). \( W_r \) is proportional to the number of random numbers with uniform distribution in \([0,1]\) produced in a single relaxation sweep. 2) The Metropolis acceptance ratio \( (MAR) \) of chain states, and 3) The integrated decorrelation times \( (\tau_{\text{int}}) \) for measurements of \( <r> \).

As seen in Table 3, for large \( N \), \( MAR \) is approximately 0.5 for \( N_c = 5 \) and \( N_{\text{try}} = 2 \). Increasing these two numbers results only in very small decrease of \( \tau_{\text{int}} \). Clearly, although the staging algorithm is much faster than a primitive Metropolis algorithm, it does not eliminate the CSD.

| \( N \) | \( \tau \) | \( N_c \) | \( N_{\text{try}} \) | \( W_r \) | \( MAR \) | \( \tau_{\text{int}} <r> \) |
|---|---|---|---|---|---|---|
| 32 | 1.0 | 4 | 1 | 0.21 | 0.32 | 15.6 |
| | | | 2 | 0.44 | 0.67 | 7.7 |
| | | | 5 | 0.64 | 0.32 | 7.8 |
| | | | 3 | 0.95 | 0.48 | 7.7 |
| | | 6 | 4 | 1.7 | 0.24 | 9.5 |
| | | | 5 | 2.1 | 0.32 | 8.5 |
| 64 | 0.5 | 4 | 1 | 0.44 | 0.45 | 33.0 |
| | | | 5 | 1.3 | 0.46 | 14.6 |
| | | | 3 | 1.9 | 0.67 | |
| | | | 6 | 2.5 | 0.31 | |
| | | | 4 | 3.3 | 0.41 | |
| | | | 5 | 4.1 | 0.50 | 12.5 |
| 128 | 0.25 | 4 | 1 | 0.86 | 0.50 | 120.0 |
| | | | 5 | 1.30 | 0.25 | |
| | | | 2 | 2.5 | 0.51 | 75.0 |
| 256 | 0.125 | 4 | 1 | 1.7 | 0.51 | |
| | | | 5 | 2.5 | 0.27 | |
| | | | 2 | 5.1 | 0.53 | 350.0 |
| 512 | 0.0625 | 5 | 2 | 10.0 | 0.53 | 1240.0 |

Table 3 - Staging algorithm
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