Numerical path integration with Coulomb potential

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Abstract

A simple and efficient method for quantum Monte Carlo simulation is presented, based on discretization of the action in the path integral, and a Gaussian averaging of the potential, which works well e.g. with the Coulomb potential. Non-integrable hard core potentials cannot be averaged in the same way.

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1 Introduction

The quantum Monte Carlo method is well established as an efficient calculational tool for many-body problems. See for example the review articles [1, 2, 3]. It is well suited for bosonic systems without magnetic field, where the path integral has only positive contributions. But also fermionic systems can be treated, in spite of the troublesome “sign problem”, just one application is the computation of the high temperature phase diagram of hydrogen [4, 5]. One limitation is that it is a statistical method, so that every factor of 10 in precision costs a factor of 100 in computing time. But it does not hit the “exponential wall”, because it only needs to represent particle positions, or particle paths, and so the number of parameters increases linearly with the number of particles.

By contrast, the number of particles that can be handled by methods based on computing realistic many-body wave functions is limited by the exponential increase in the number of parameters needed for describing such wave functions. The density functional method [6] is less severely limited, since it uses one particle wave functions, but on the other hand it has to rely on clever approximation techniques.

The purpose of the work presented here was to look for a simple and efficient way of handling the Coulomb potential in quantum Monte Carlo simulation. Formulae for the exact propagator of the two-particle Coulomb problem are known, and can even be derived by path integral methods [7, 8], but it is not clear whether they are useful for the simulation of many-body systems. In ref. [4] fitted formulae for two-particle propagators were used. This may be a good enough method, but it may nevertheless be of interest to look for more direct approaches.

The Fourier representation of paths in path integrals was introduced by Feynman, together with the idea of approximately integrating over infinitely many Fourier components.
by averaging the potential \[9\]. The method was further developed by Doll, Coalson, and Freeman \[10, 11\] under the name of partial averaging. In their work and in subsequent work, see e.g. \[12, 13\], the object focused upon has been the propagator, involving paths from one point to another, more than the partition function, involving closed paths.

The basic idea is to let the path integral include only paths represented by finite Fourier series with a fixed number of terms, and to think of each such path as representing all the infinite Fourier series to which it can be extended. The result is that, as long as correlations along the path are neglected, each point on one truncated path represents a Gaussian distribution of points, with a standard deviation decreasing from the middle of the path and vanishing at the end points. In the case of the Coulomb potential, the Gaussian averaging has the important effect of removing the singularity at zero distance. It is then a complication that the averaging varies along the path, disappearing towards the end points \[13\].

The modification proposed here is to average with a standard deviation which is constant along the path. This seems a natural approach when the partition function is computed directly, and not via the propagator. In more detail, the method proposed amounts to a discretization of the action integral, with an averaged potential, and the computation of the kinetic energy part of the action by means of a finite Fourier transform. As discussed below, within this method it is easy to add to any potential an auxiliary confining harmonic oscillator potential, which makes the partition function mathematically well defined.

A different topic which is not addressed here is the optimization of the Monte Carlo sampling procedure. See in this connection the comment in an appendix of ref. \[13\]. A finite Fourier transform is a central part of the present method. In the method as formulated here it is assumed that the number of time steps is odd, hence the standard fast Fourier transform with \(2^n\) points, \(n = 1, 2, \ldots\), can not be used. One solution is to use \(3^n\) points and the fast Fourier transform to base three \[14\]. However, it would also be straightforward to modify the method so as to use an even number of time steps.

## 2 The imaginary time path integral

Equilibrium properties of a physical system at a finite temperature \(T\) can be computed from the partition function

\[
Z(\beta) = \text{Tr} e^{-\beta H},
\]

where \(H\) is the Hamiltonian, and \(\beta = 1/(k_B T)\). One may regard \(\beta\hbar\) formally as an imaginary time interval.

To be specific, we consider most of the time one particle of mass \(m\) in three dimensions. The Hamiltonian is \(H = T + V\), with \(T = p^2/(2m)\) the kinetic energy and \(V = V(r)\) the potential energy. The partition function has the following path integral representation,

\[
Z = \tilde{C}_0^3 \int d^3a_0 \prod_{n=1}^{\infty} \left( \tilde{C}_n^6 \int d^6a_n \right) \exp\left( -\frac{S}{\hbar} \right).
\]

We define the constants

\[
C_0 = \frac{1}{\hbar} \sqrt{\frac{m}{2\beta}}, \quad C_n = \frac{2n\pi}{\hbar} \sqrt{\frac{m}{\beta}} \quad \text{for} \quad n = 1, 2, \ldots,
\]
and $\tilde{C}_n = C_n / \sqrt{\pi}$ for $n = 0, 1, 2, \ldots$. $S$ is the imaginary time action, 

$$S = \frac{1}{\hbar} \int_0^{\beta \hbar} d\tau \left( \frac{1}{2} m (\dot{r}(\tau))^2 + V(r(\tau)) \right) = \sum_{n=1}^{\infty} C_n^2 |a_n|^2 + \frac{1}{\hbar} \int_0^{\beta \hbar} d\tau V(r(\tau)) . \quad (4)$$

The path $r = r(\tau)$ is periodic in the imaginary time $\tau$, with period $\beta \hbar$, and is given by the infinite Fourier series 

$$r(\tau) = \sum_{n=-\infty}^{\infty} a_n e^{i \frac{2n \pi}{\beta \hbar} \tau} . \quad (5)$$

The Fourier components $a_n$ are complex and satisfy the relations $a_{-n} = a_n^*$, so that $r(\tau)$ is real. In particular, $a_0$ is real. The time derivative $\dot{r}$ is with respect to the imaginary time $\tau$.

This Fourier expansion is the natural one in the computation of the partition function, which involves periodic paths. A slightly different expansion is needed in the computation of propagators, see e.g. [9, 10, 11, 12, 13].

It may be useful to sketch the derivation of this Fourier path integral. We start from the approximation

$$Z \approx \text{Tr} \left( e^{-\frac{S}{\hbar}} \prod_{j=1}^{J} \left( e^{-\frac{\beta}{\hbar} T} e^{-\frac{\beta}{\hbar} V} \right) \right) . \quad (6)$$

We insert $J$ times the identity operator $I = \int d^3 r |r\rangle\langle r|$ where $|r\rangle$ is the position eigenstate, and introduce the free particle propagator

$$\langle r'| e^{-\beta T} |r \rangle = \tilde{C}_0 e^{-C_0^2 |r-r'|^2} , \quad (7)$$

to obtain the approximation

$$Z \approx \left( \sqrt{J} \tilde{C}_0 \right)^{3J} \int d^3 r_1 d^3 r_2 \cdots d^3 r_J \exp \left( -\frac{S_P}{\hbar} \right) . \quad (8)$$

Here $S_P$ is the “primitive” discretized action defined by

$$S_P = \frac{\hbar}{J} \sum_{j=1}^{J} |r_j - r_{j+1}|^2 + \frac{\beta}{J} \sum_{j=1}^{J} V(r_j) . \quad (9)$$

We define $r_{J+1} = r_1$. This approximate expression for $Z$ is exact when $V = 0$, and gives then in particular for $J = 1$ that

$$Z = \tilde{C}_0 e^{C_0^2} \int d^3 r_1 . \quad (10)$$

To make this integral finite we should regularize, e.g. by introducing periodic boundary conditions or an external harmonic oscillator potential. See Section 7 below.

We now take $J$ to be odd, $J = 2K + 1$, and make the finite Fourier transform

$$r_j = \sum_{n=-K}^{K} a_n e^{i \frac{2n \pi}{2K+1} j} . \quad (11)$$
It gives that

\[ \frac{S_P}{\hbar} = \sum_{n=1}^{\infty} C_{n,K}^2 |a_n|^2 + \frac{\beta}{J} \sum_{j=1}^{J} V(r_j), \]  

(12)

with, for \( n = 1, 2, \ldots \),

\[ C_{n,K} = \frac{2(2K+1)}{\hbar} \sqrt{\frac{m}{\beta}} \sin\left(\frac{n\pi}{2K+1}\right), \quad \tilde{C}_{n,K} = \frac{C_{n,K}}{\sqrt{\pi}}. \]  

(13)

In order to transform the integral over the positions \( r_j \) into an integral over the Fourier components \( a_n \), we note that

\[ \sum_j |d r_j|^2 = (2K+1) \left( |d a_0|^2 + 2 \sum_{n=1}^{K} |d a_n|^2 \right), \]  

(14)

and hence,

\[ \prod_j d^3 r_j = 2^{3K} \left( \sqrt{2K+1} \right)^{3(2K+1)} d^3 a_0 \prod_{n=1}^{K} d^6 a_n. \]  

(15)

Using the identity

\[ \sqrt{2K+1} = 2^K \prod_{n=1}^{K} \sin\left(\frac{n\pi}{2K+1}\right), \]  

(16)

we rewrite Equation (8) as follows,

\[ Z \approx \tilde{C}_0^3 \int d^3 a_0 \left( \prod_{n=1}^{K} \tilde{C}_{n,K}^6 \int d^6 a_n \right) \exp\left(-\frac{S_P}{\hbar}\right). \]  

(17)

The limit \( K \to \infty \) gives Equation (2). We regard \( r_j \) as a function of the variable \( \tau = j\beta\hbar/(2K+1) \), which becomes continuous in the limit.

3 Averaging the potential

The integrand of the path integral, Equation (2), is the negative exponential of \( S/\hbar \), Equation (4). One way to interpret this is that the kinetic part of \( S \) defines independent Gaussian probability distributions for the Fourier coefficients \( a_n, n > 0 \), such that the real and imaginary parts of the \( x, y, z \) components of \( a_n \) have mean values zero and standard deviations

\[ \sigma_n = \frac{1}{\sqrt{2C_n}} = \frac{\hbar}{2n\pi} \sqrt{\frac{\beta}{2m}}. \]  

(18)

The path integral may be computed approximately by the partial averaging method [10, 11]. We integrate explicitly over the lowest Fourier components, and approximate the integral
over the infinite number of remaining coefficients simply by averaging the potential. This means that we choose some finite $K$ and define

$$R(\tau) = \sum_{n=-K}^{K} a_n e^{i \frac{2n\pi}{\beta h}}. \quad (19)$$

The remainder term $s(\tau) = r(\tau) - R(\tau)$ will have a Gaussian distribution with zero mean and with variances

$$\langle (s_x(\tau))^2 \rangle = \langle (s_y(\tau))^2 \rangle = \langle (s_z(\tau))^2 \rangle = \frac{\langle s(\tau)^2 \rangle}{3} = \sigma^2. \quad (20)$$

To compute $\sigma$, we compute

$$\frac{\langle s(\tau_1) \cdot s(\tau_2) \rangle}{3} = \frac{\beta h^2}{2\pi^2 m} \sum_{n=K+1}^{\infty} \frac{1}{n^2} \cos\left(\frac{2n\pi(\tau_1 - \tau_2)}{\beta h}\right) = \frac{\beta h^2}{2\pi^2 m} f_K\left(\frac{\tau_1 - \tau_2}{\beta h}\right), \quad (21)$$

where the function $f_K = f_K(u)$ has period 1 in its argument $u$,

$$f_K(u) = \sum_{n=K+1}^{\infty} \frac{\cos(2n\pi u)}{n^2} = \pi^2 \left(u - \frac{1}{2}\right)^2 - \frac{\pi^2}{12} - \sum_{n=1}^{K} \frac{\cos(2n\pi u)}{n^2}. \quad (22)$$

The last formula is valid for $0 \leq u \leq 1$. Thus we have

$$\sigma^2 = \frac{\beta h^2}{2\pi^2 m} f_K(0) = \frac{\beta h^2}{2\pi^2 m} \left(\pi^2 \left(\frac{1}{6} - \sum_{n=1}^{K} \frac{1}{n^2}\right)\right) \approx \frac{\beta h^2}{(2K + 1)\pi^2 m}, \quad (23)$$

introducing the approximation

$$\sum_{n=K+1}^{\infty} \frac{1}{n^2} \approx \int_{K+\frac{1}{2}}^{\infty} \frac{dn}{n^2} = \frac{2}{2K + 1}, \quad (24)$$

which is about 20% larger than the exact result $\pi^2/6$ in the worst case $K = 0$.

The problem facing us is to compute the integral

$$I = \prod_{n=K+1}^{\infty} \left(C_n^6 \int d^6 a_n \exp\left(-C_n^2 |a_n|^2\right)\right) \exp\left(-\frac{1}{h} \int_0^{\beta h} d\tau \, V(r(\tau))\right). \quad (25)$$

Here $r(\tau) = R(\tau) + s(\tau)$ is given by Equation (5), and $R(\tau)$ by Equation (19). To simplify our notation, we write the integral as an average. Next, we assume that $s(\tau_1)$ and $s(\tau_2)$ are uncorrelated for $\tau_1 \neq \tau_2$, which is true to a certain approximation, as shown by Equation (21).

In this approximation we may compute the integral by the following formal reasoning,

$$I = \left\langle \exp\left(-\frac{1}{h} \int_0^{\beta h} d\tau \, V(r(\tau))\right) \right\rangle = \left\langle \prod_{\tau=0}^{\beta h} \exp\left(-\frac{d\tau}{h} \, V(r(\tau))\right) \right\rangle$$

$$\approx \prod_{\tau=0}^{\beta h} \left(1 - \frac{d\tau}{h} V(r(\tau))\right) = \exp\left(-\frac{1}{h} \int_0^{\beta h} d\tau \, W(R(\tau))\right) , \quad (26)$$
where $W$ is an averaged version of the potential $V$,

$$W(R) = \langle V(r) \rangle = \langle V(R + s) \rangle = \frac{1}{\sqrt{2\pi}\sigma} \int d^3s \ e^{-\frac{s^2}{2\sigma^2}} V(R + s).$$  \hspace{1cm} (27)$$

The standard deviation $\sigma$ is given by Equation (23). Note that the effective potential $W$ depends on $K$, since $\sigma$ depends on $K$.

To summarize, we propose the approximation

$$Z \approx \tilde{C}_0^3 \int d^3a_0 \left( \prod_{n=1}^K \tilde{C}_n \int d^6a_n \right) \exp \left( -\frac{S_A}{\hbar} \right),$$  \hspace{1cm} (28)$$

where

$$S_A = \sum_{n=1}^K C_n^2 |a_n|^2 + \frac{1}{\hbar} \int_0^{\beta\hbar} d\tau W(R(\tau)).$$  \hspace{1cm} (29)$$

The most drastic approximation is of course to take $K = 0$, see [9]. Then we get

$$\sigma = \sqrt{\frac{\beta\hbar^2}{12m}},$$  \hspace{1cm} (30)$$

and

$$Z \approx \left( \frac{m}{2\pi\beta\hbar} \right)^{\frac{3}{2}} \int d^3a_0 \ \exp(-\beta W(a_0)).$$  \hspace{1cm} (31)$$

The present version of the partial averaging method is simpler than the original one [10, 11, 12, 13], in that the standard deviation $\sigma$ is taken to be constant. The method has been used previously for computing the propagator, and not directly the partition function. Then $\sigma$ has to vary along the path, since it must vanish at the end points.

4 Example 1: The harmonic oscillator

If $V$ is a harmonic oscillator potential,

$$V(r) = \frac{1}{2} m\omega^2 r^2,$$  \hspace{1cm} (32)$$

then the averaged potential $W$ is just $V$ plus a constant,

$$W(r) = V(r) + \frac{3}{2} m\omega^2 \sigma^2.$$  \hspace{1cm} (33)$$

The addition to the potential contributes a multiplicative factor in the partition function, and the resulting approximation is

$$Z \approx \exp \left( -\frac{3(\beta\hbar\omega)^2}{4\pi^2} \left( \frac{\pi^2}{6} - \sum_{n=1}^K \frac{1}{n^2} \right) \right) \frac{1}{(\beta\hbar\omega)^3} \prod_{n=1}^K \left( 1 + \left( \frac{\beta\hbar\omega}{2n\pi} \right)^2 \right)^{-3}. $$  \hspace{1cm} (34)$$

Another way to obtain the same approximation is to set

$$1 + \left( \frac{\beta\hbar\omega}{2n\pi} \right)^2 \approx \exp \left( \left( \frac{\beta\hbar\omega}{2n\pi} \right)^2 \right) $$  \hspace{1cm} (35)$$

for $n > K$, in Equation (34) with $B = 0$, this is valid when we choose $K$ large enough that

$$\frac{\beta\hbar\omega}{2K\pi} \ll 1.$$  \hspace{1cm} (36)$$
5 Example 2: The Coulomb potential

Consider now two particles of masses $m_1, m_2$ and charges $q_1, q_2$, interacting by the Coulomb potential

$$V = V(r_1, r_2) = \frac{q_1 q_2}{4\pi \epsilon_0 |r_1 - r_2|}. \quad (37)$$

We write Fourier expansions for the paths of both particles,

$$r_1(\tau) = \sum_{n=-\infty}^{\infty} a_{1n} e^{i \frac{2\pi n}{\beta} \tau}, \quad r_2(\tau) = \sum_{n=-\infty}^{\infty} a_{2n} e^{i \frac{2\pi n}{\beta} \tau}. \quad (38)$$

The partition function is

$$Z = \left( \frac{\sqrt{m_1 m_2}}{2\pi \hbar^2} \right)^3 \int d^3a_{10} d^3a_{20} \left( \prod_{n=1}^{\infty} \left( \frac{4n^2 \pi \sqrt{m_1 m_2}}{\beta \hbar^2} \right)^6 \int d^6a_{1n} d^6a_{2n} \right) \exp \left( -\frac{S}{\hbar} \right), \quad (39)$$

where

$$S = \int_{0}^{\beta \hbar} d\tau \left( \frac{1}{2} m_1 (\dot{r}_1(\tau))^2 + \frac{1}{2} m_2 (\dot{r}_2(\tau))^2 + V(r_1(\tau), r_2(\tau)) \right)$$

$$= \frac{4\pi^2}{\beta \hbar} \sum_{n=1}^{\infty} n^2 (m_1 |a_{1n}|^2 + m_2 |a_{2n}|^2) + \int_{0}^{\beta \hbar} d\tau V(r(\tau)). \quad (40)$$

The potential depends only on the relative position

$$r(\tau) = r_1(\tau) - r_2(\tau) = \sum_{n=-\infty}^{\infty} a_n e^{i \frac{2\pi n}{\beta} \tau}, \quad (41)$$

where $a_n = a_{1n} - a_{2n}$. The real and imaginary parts of the $x, y, z$ components of the Fourier coefficients $a_n$ have mean values zero and standard deviations

$$\sigma_n = \sqrt{\frac{\langle |a_{1n}|^2 \rangle + \langle |a_{2n}|^2 \rangle}{6}} = \frac{\hbar}{2n\pi} \sqrt{\frac{\beta}{2m}}, \quad (42)$$

where $m$ is the reduced mass,

$$\frac{1}{m} = \frac{1}{m_1} + \frac{1}{m_2}. \quad (43)$$

Like in the one particle case, we define $R(\tau)$ by an equation of the same form as Equation (19). We integrate explicitly over the Fourier coefficients $a_{1n}$ and $a_{2n}$ up to $n = K$, and we do the remaining integrations approximately by averaging the potential as in Equation (27). The averaged Coulomb potential is

$$W(r) = \frac{q_1 q_2}{4\pi \epsilon_0 r} \operatorname{erf} \left( \frac{r}{\sqrt{2\sigma}} \right). \quad (44)$$

It equals the Coulomb potential in the limit $r \to \infty$, but is nonsingular at the origin. The standard deviation $\sigma$ is defined as in Equation (28), now with $m$ as the reduced mass. The effect of the averaging is a multiplication by the error function, defined as

$$\operatorname{erf}(x) = \frac{2}{\sqrt{\pi}} \int_{0}^{x} du e^{-u^2}. \quad (45)$$
### Table 1: Zeros of the correlation functions $f_K(u)$, with $0 < u < 1/2$, multiplied by $2K + 1$.

| $K$ | 1   | 2    | 3    | 4    | 5    |
|-----|-----|------|------|------|------|
| 0   | 0.211 | 1.068 |      |      |      |
| 1   | 0.265 | 1.110 | 2.032 |      |      |
| 2   | 0.276 | 1.123 | 2.059 | 3.018 |      |
| 3   | 0.277 | 1.128 | 2.070 | 3.036 | 4.011 |
| 4   | 0.278 | 1.131 | 2.075 | 3.045 | 4.024 |
| 5   | 0.278 | 1.135 | 2.083 | 3.058 | 4.042 |
| 10  | 0.278 | 1.136 | 2.086 | 3.061 | 4.047 |
| 20  | 0.279 | 1.136 | 2.086 | 3.062 | 4.048 |
| 50  | 0.279 | 1.137 | 2.086 | 3.062 | 4.048 |

6 Numerical computation

A numerical estimate of the action $S_A$ with the averaged potential $W$ is the completely discretized action $S_D$ defined by

$$
\frac{S_D}{\hbar} = \sum_{n=1}^{K} C_n^2 |a_n|^2 + \frac{\beta}{2K + 1} \sum_{j=0}^{2K} W(r_j),
$$

(46)

where the positions $r_j$ are given by the Fourier coefficients according to Equation (11).

There are at least three arguments in favour of choosing exactly $2K + 1$ evaluation points for the action integral of the potential. One is that this replacement of the integral by a sum is exact for a constant, linear or quadratic potential. Another argument is that the real Fourier coefficient $a_0$ and the $K$ complex Fourier coefficients $a_1, \ldots, a_K$ are just what is needed to fix the $2K + 1$ positions $r_j$.

The third argument is less obvious. In fact, our justification of the averaging procedure defining $W$ suggests that the evaluation points $\tau_j$ should be chosen in such a way that the covariances $\langle s(\tau_j) \cdot s(\tau_k) \rangle$, given by Equation (21), are small. These covariances are proportional to the function $f_K(u)$ given in Equation (22), which is symmetric about $u = 1/2$, and has $K + 1$ zeros between 0 and 1/2. Of these zeros, $K$ are close to the values $u_j = j/(2K + 1)$, for $j = 1, 2, \ldots, K$, as Table 1 shows. Thus, with $2K + 1$ equally spaced points $\tau_j$ we have that $\langle s(\tau_j) \cdot s(\tau_k) \rangle \approx 0$ for $j \neq k$.

This does not necessarily forbid us to use for example twice as many evaluation points. We may define $\Delta \tau = \beta \hbar/(2K + 1)$ and

$$
S_a = \Delta \tau \sum_{j=0}^{2K} W(R(j \Delta \tau)) , \quad S_b = \Delta \tau \sum_{j=0}^{2K} W(R((j + \frac{1}{2}) \Delta \tau)) .
$$

(47)

But if we do so, we should perhaps compute $(e^{-S_a} + e^{-S_b})/2$ rather than $e^{-S_a} e^{-S_b}$.

To summarize again, the numerical approximation proposed here is based on evaluation of the following integral, where $S_D$ is the discrete action defined in Equation (46),

$$
Z \approx \bar{C}_0^3 \int d^3a_0 \left( \prod_{n=1}^{K} \bar{C}_n^6 \int d^6a_n \right) \exp\left( -\frac{S_D}{\hbar} \right) .
$$

(48)
From the partition function we compute the expectation value of the energy as

\[ E = \langle H \rangle = -\frac{\partial}{\partial \beta} \ln Z(\beta). \]  \hspace{1cm} (49)

In the above approximate partition function there is \( \beta \) dependence in the coefficients \( C_n \) and \( \tilde{C}_n \), and also in the averaged potential \( W \). We get that

\[ E \approx \frac{3(2K + 1)}{2\beta} + \frac{\int d^3a_0 \left( \prod_{n=1}^{K} \int d^6a_n \right) \exp \left( -\frac{\mathcal{S}_D}{\hbar} \right) \frac{1}{\hbar} \frac{\partial \mathcal{S}_D}{\partial \beta}}{\int d^3a_0 \left( \prod_{n=1}^{K} \int d^6a_n \right) \exp \left( -\frac{\mathcal{S}_D}{\hbar} \right)}, \]  \hspace{1cm} (50)

and

\[ \frac{1}{\hbar} \frac{\partial \mathcal{S}_D}{\partial \beta} = -\frac{1}{\beta} \sum_{n=1}^{K} C_n^2 |a_n|^2 + \frac{1}{2K + 1} \sum_{j=0}^{2K} \left( W(r_j) + \beta \frac{\partial}{\partial \beta} W(r_j) \right). \]  \hspace{1cm} (51)

Note that Equation (50) may be rewritten as

\[ E \approx \frac{3(2K + 1)}{2\beta} + \frac{\left( \prod_{j=0}^{2K} \int d^3r_j \right) \exp \left( -\frac{\mathcal{S}_D}{\hbar} \right) \frac{1}{\hbar} \frac{\partial \mathcal{S}_D}{\partial \beta}}{\left( \prod_{j=0}^{2K} \int d^3r_j \right) \exp \left( -\frac{\mathcal{S}_D}{\hbar} \right)}. \]  \hspace{1cm} (52)

Here the Fourier coefficients are present only in the kinetic part of the discrete action \( S_D \).

In general we have that

\[ \beta \frac{\partial}{\partial \beta} W(r) = \beta \frac{\partial \sigma}{\partial \beta} \frac{\partial}{\partial \sigma} W(r) = \sigma \frac{\partial}{\partial \sigma} W(r). \]  \hspace{1cm} (53)

Hence we get, in the example of the harmonic oscillator potential, Equation (33),

\[ \beta \frac{\partial}{\partial \beta} W(r) = \frac{3}{2} m\omega^2 \sigma^2. \]  \hspace{1cm} (54)

And in the example of the Coulomb potential, Equation (44),

\[ \beta \frac{\partial}{\partial \beta} W(r) = -\frac{q_1 q_2}{4\pi \epsilon_0 (\sqrt{2\pi} \sigma)} \exp \left( -\frac{r^2}{2\sigma^2} \right). \]  \hspace{1cm} (55)

In the approximate expression for \( \langle H \rangle = \langle T \rangle + \langle V \rangle \) it is not immediately obvious which contributions represent kinetic and potential energy, respectively. In order to identify the different terms, we should define

\[ Z(\beta_1, \beta_2) = \text{Tr} e^{-\beta_1 T - \beta_2 V}, \]  \hspace{1cm} (56)

and use that, e.g.,

\[ \langle V \rangle = -\frac{\partial}{\partial \beta_2} \ln Z(\beta_1, \beta_2) \bigg|_{\beta_1 = \beta_2 = \beta}. \]  \hspace{1cm} (57)

This formula holds because

\[ \frac{\partial}{\partial \beta_2} e^{-\beta_1 T - \beta_2 V} = -\int_0^1 d\lambda e^{-\lambda(\beta_1 T + \beta_2 V)} V e^{-(1-\lambda)(\beta_1 T + \beta_2 V)}, \]  \hspace{1cm} (58)
and hence

\[ \frac{\partial}{\partial \beta_2} Z(\beta_1, \beta_2) = - \text{Tr}(V e^{-\beta_1 T - \beta_2 V}). \]  

(59)

The somewhat surprising conclusion is that

\[ \langle V \rangle \approx \left( \prod_{j=0}^{2K} \int d^3 r_j \right) \exp \left( - S_D \frac{\bar{\hbar}}{2} \sum_{j=0}^{2K} W(r_j) \right), \]

whereas \( \langle T \rangle \) is all the rest of the right hand side of Equation (50) or Equation (52).

For bound states of any number of particles, with the Coulomb interaction, the virial theorem states that \( 2 \langle T \rangle + \langle V \rangle = 0 \). It gives a good check on numerical results for bound states, if one computes both \( \langle T \rangle \) and \( \langle V \rangle \). It may also be used to (potentially) improve the precision of computed energies, since it implies for example that

\[ E = \langle T \rangle + \langle V \rangle = -\langle T \rangle = \frac{\langle V \rangle}{2}. \]  

(61)

The statistical error with which the two expectation values \( \langle T \rangle \) and \( \langle V \rangle \) are computed in a Monte Carlo simulation will in general not be the same, hence one may use whichever value has the smallest error.

## 7 Regularization

For simplicity, we have so far neglected the fact that the partition function is not mathematically well defined for a system in an infinite volume when, for example, the potential goes to zero at infinity, like the Coulomb potential. In our present context, the problem is that the integral over \( a_0 \) diverges. In practice, when the integral is computed by some Monte Carlo method using a random walk algorithm of the Metropolis type, the divergence means that there is a finite probability of walking away to infinity, where the potential vanishes. This may be no problem in practice, because the divergence may be so improbable that it will never happen in the Monte Carlo simulation. Nevertheless, one may like to introduce some kind of regularization which makes the partition function well defined.

A convenient regularization method in our case is to add to the Hamiltonian an extra harmonic oscillator potential

\[ V_0(r) = \frac{1}{2} m \omega_0^2 r^2, \]  

(62)

with a suitably chosen angular frequency \( \omega_0 \). The Fourier expansion of Equation (5) implies that

\[ \frac{1}{\hbar} \int_0^{\beta\hbar} d\tau V_0(r(\tau)) = \frac{\beta m \omega_0^2}{2} \left( |a_0|^2 + 2 \sum_{n=1}^{\infty} |a_n|^2 \right). \]  

(63)

Hence, Equation (41) is modified to read

\[ S = \sum_{n=0}^{\infty} D_n^2 |a_n|^2 + \frac{1}{\hbar} \int_0^{\beta\hbar} d\tau V(r(\tau)), \]  

(64)
where
\[ D_0^2 = \frac{\beta m \omega_0^2}{2}, \quad D_n^2 = C_n^2 + \beta m \omega_0^2 = \frac{4(n^2 + \nu^2)\pi^2 m}{\beta \hbar^2}, \tag{65} \]
for \( n = 1, 2, \ldots \), and
\[ \nu = \frac{\beta \hbar \omega_0}{2\pi}. \tag{66} \]

We define also \( \bar{D}_n = D_n / \sqrt{\pi} \) for \( n = 0, 1, 2, \ldots \). Since
\[ \frac{\bar{C}_0}{D_0} \prod_{n=1}^{\infty} \frac{\bar{C}_n^2}{D_n^2} = \frac{1}{\beta \hbar \omega_0} \prod_{n=1}^{\infty} \frac{n^2}{n^2 + \nu^2} = \frac{1}{2 \sinh(\nu \pi)}, \tag{67} \]
we may rewrite Equation (2) as
\[ Z = Z_0 \bar{D}_0^3 \int d^3a_0 \prod_{n=1}^{\infty} \left( \bar{D}_n^6 \int d^6a_n \right) \exp \left( -\frac{S}{\hbar} \right), \tag{68} \]
where \( Z_0 \) is the partition function of the three dimensional harmonic oscillator with angular frequency \( \omega_0 \),
\[ Z_0 = Z_0(\beta) = \frac{1}{8 \sinh^3(\nu \pi)}. \tag{69} \]

This expression for the partition function \( Z = Z(\beta) \) is mathematically well defined, when the harmonic oscillator potential \( V_0 \) is included in addition to the potential \( V \), so that Equation (64) holds.

A natural way to interpret Equation (68) is that the Fourier coefficients \( a_n \) are Gaussian random variables with mean zero and standard deviations \( \sigma_n = 1 / \sqrt{2 D_n} \). Our derivation of how to replace the potential \( V \) by an averaged potential \( W \), goes through with little change. The most important change is that the denominator \( n^2 \) in Equation (21) has to be replaced by \( n^2 + \nu^2 \), and hence the correlation function \( f_K \) is replaced by a function \( f_{K,\nu} \) which is still periodic with period 1,
\[ f_{K,\nu}(u) = \sum_{n=K+1}^{\infty} \frac{\cos(2n\pi u)}{n^2 + \nu^2} = \frac{\pi \cosh(\nu \pi (2u - 1))}{2\nu \sinh(\nu \pi)} - \frac{1}{2\nu^2} - \sum_{n=1}^{K} \frac{\cos(2n\pi u)}{n^2 + \nu^2}, \tag{70} \]
the last formula being valid for \( 0 \leq u \leq 1 \). The zeros of \( f_{K,\nu} \) between 0 and 1/2 are even closer to the values \( u_k = k/(2K + 1) \), for \( k = 1, 2, \ldots, K \), than those of \( f_K \), as Table 2 shows, for the arbitrarily chosen value \( \nu = 10 \).

The numerical computation now involves the following modified version of Equation (48),
\[ Z \approx Z_0 \bar{D}_0^3 \int d^3a_0 \prod_{n=1}^{K} \left( \bar{D}_n^6 \int d^6a_n \right) \exp \left( -\frac{S_D}{\hbar} \right), \tag{71} \]
where we use also a modified definition of the discrete action \( S_D \),
\[ \frac{S_D}{\hbar} = \sum_{n=0}^{K} D_n^2 |a_n|^2 + \frac{\beta}{2K + 1} \sum_{j=0}^{2K} W(r_j) \]
\[ = \sum_{n=1}^{K} C_n^2 |a_n|^2 + \frac{\beta}{2K + 1} \sum_{j=0}^{2K} (V_0(r_j) + W(r_j)). \tag{72} \]
| $K$ | 1   | 2   | 3   | 4   | 5   |
|-----|-----|-----|-----|-----|-----|
| 0   | 0.055 |   |   |   |   |
| 1   | 0.113 | 1.003 |   |   |   |
| 2   | 0.151 | 1.011 | 2.002 |   |   |
| 3   | 0.177 | 1.035 | 2.015 | 3.007 | 4.002 |
| 4   | 0.197 | 1.048 | 2.021 | 3.012 | 4.006 |
| 5   | 0.211 | 1.093 | 2.050 | 3.033 | 4.023 |
| 10  | 0.249 | 1.093 | 2.050 | 3.033 | 4.023 |
| 20  | 0.269 | 1.122 | 2.073 | 3.051 | 4.038 |
| 50  | 0.277 | 1.134 | 2.084 | 3.060 | 4.046 |

Table 2: Zeros of the correlation functions $f_{K,\nu}(u)$, with $0 < u < 1/2$, multiplied by $2K + 1$. The table is for $\nu = 10$.

The standard deviation $\sigma$ to be used in the definition of the averaged potential $W$, will now be given by the formula

$$\sigma^2 = \frac{\beta \hbar^2}{2\pi^2 m} f_{K,\nu}(0) = \frac{\beta \hbar^2}{2\pi^2 m} \left( \frac{\pi \coth(\nu \pi)}{2\nu} - \frac{1}{2\nu^2} - \sum_{n=1}^{K} \frac{1}{n^2 + \nu^2} \right). \tag{73}$$

Using Equation (71), we compute the total energy $\langle E \rangle = \langle T \rangle + \langle V \rangle + \langle V_0 \rangle$ as

$$\langle E \rangle = -\frac{\partial}{\partial \beta} \ln Z \approx \frac{3(2K + 1)}{2\beta} + \frac{6\nu^2}{\beta} f_{K,\nu}(0) + \frac{\left( \prod_{j=0}^{2K} \int d^3r_j \right) \exp\left( -\frac{S_D}{\hbar} \right) \frac{1}{\hbar} \frac{\partial S_D}{\partial \beta}}{\left( \prod_{j=0}^{2K} \int d^3r_j \right) \exp\left( -\frac{S_D}{\hbar} \right)} \tag{74}.$$ 

Compare this to Equation (52). The modified version of Equation (51) is the following,

$$\frac{1}{\hbar} \frac{\partial S_D}{\partial \beta} = -\frac{1}{\beta} \sum_{n=1}^{K} C_n^2 |a_n|^2 + \frac{1}{2K + 1} \sum_{j=0}^{2K} \left( V_0(r_j) + W(r_j) + \beta \frac{\partial}{\partial \beta} W(r_j) \right). \tag{75}$$

Equation (73) gets modified as follows,

$$\beta \frac{\partial}{\partial \beta} W(r) = \left( 1 + \nu \frac{\partial}{\partial \nu} \ln f_{K,\nu}(0) \right) \frac{\sigma}{2} \frac{\partial}{\partial \sigma} W(r). \tag{76}$$

In order to calculate separately the expectation values $\langle T \rangle$, $\langle V \rangle$, and $\langle V_0 \rangle$, we should define

$$Z = Z(\beta_0, \beta_1, \beta_2) = \text{Tr} e^{\beta_1 T - \beta_2 V - \beta_0 V_0}, \tag{77}$$

and keep track of the three parameters $\beta_0, \beta_1, \beta_2$ before setting them all equal to $\beta$. This gives for $\langle V \rangle$ a formula exactly like Equation (60). An easier way to compute $\langle V_0 \rangle$ is to note that

$$\langle V_0 \rangle = -\frac{\omega_0}{2\beta} \frac{\partial}{\partial \omega_0} \ln Z \approx \frac{3\nu^2}{\beta} f_{K,\nu}(0) + \frac{\left( \prod_{j=0}^{2K} \int d^3r_j \right) \exp\left( -\frac{S_D}{\hbar} \right) \frac{\omega_0}{2\hbar} \frac{\partial S_D}{\partial \omega_0}}{\left( \prod_{j=0}^{2K} \int d^3r_j \right) \exp\left( -\frac{S_D}{\hbar} \right)}. \tag{78}$$
Here we have that
\[
\frac{\omega_0}{2\beta \hbar} \frac{\partial S_D}{\partial \omega_0} = \frac{1}{(2K + 1)} \sum_{j=0}^{2K} \left( V_0(r_j) + \frac{\omega_0}{2} \frac{\partial}{\partial \omega_0} W(r_j) \right),
\]
with
\[
\frac{\omega_0}{2} \frac{\partial}{\partial \omega_0} W(r) = \frac{\omega_0}{2} \frac{\partial \sigma}{\partial \omega_0} \frac{\partial}{\partial \sigma} W(r) = \left( \nu \frac{\partial}{\partial \nu} \ln f_{K,\nu}(0) \right) \left( \sigma \frac{\partial}{\partial \sigma} W(r) \right).
\]
Once we know \( \langle E \rangle \), \( \langle V \rangle \) and \( \langle V_0 \rangle \), we know also \( \langle T \rangle = \langle E \rangle - \langle V \rangle - \langle V_0 \rangle \). The identification of the various contributions to the total energy \( \langle E \rangle \) is seen to be not entirely trivial.

If \( V \) is taken to be the Coulomb potential, the virial theorem gives now that
\[
2 \langle T \rangle + \langle V \rangle - 2 \langle V_0 \rangle = 0.
\]
This holds for any number of particles. It provides a check on numerical results, and it may be used to compute the total energy, including the regulator potential, as
\[
E = \langle T \rangle + \langle V \rangle + \langle V_0 \rangle = \frac{\langle V \rangle}{2} + 2\langle V_0 \rangle.
\]
The energy including the Coulomb potential but excluding the regulator potential, is
\[
E_C = \langle T \rangle + \langle V \rangle = \frac{\langle V \rangle}{2} + \langle V_0 \rangle.
\]

8 Numerical test results

Table 3 presents numerical results for the ground state energy of the hydrogen atom, for comparison with the exact value of \(-13.598\) eV. All results are for a temperature of 15\,000 K.

The Monte Carlo method was used with a standard Metropolis algorithm. In each Monte Carlo step, one point to be updated is chosen randomly among the \( 2K + 1 \) points on the discrete path, then a random step is generated and either accepted or rejected depending on the change in the discrete action, \( \Delta S_D \). If \( \Delta S_D \leq 0 \), the step is accepted. If \( \Delta S_D > -\hbar \ln u \), with \( u \) a uniform random variable between 0 and 1, the step is rejected. The optimization of the Monte Carlo strategy was not considered, but is of course an important problem. In fact, the naive approach of updating one point at a time has a disastrously slow convergence when more than about one hundred time steps are used.

The main computational cost of updating one point is computing the change in the Fourier components, this takes approximately \( 2K+1 \) floating point operations. If more than one point is updated in each step, one may choose e.g. \( 2K + 1 = 3^n \) for some power \( n \), and then use the fast Fourier transform with base 3.

By far the highest statistics, \( 10^{10} \) MC steps, was run for the entry with 201 time steps. In this case, statistical uncertainties are given in the table, and the values found for the ground state energy are consistent with the exact value, within the uncertainties of less than one per cent. A number of time steps of the order of 50 may give sufficient accuracy for many purposes.

It is noteworthy that the statistical error in the direct estimate of the energy, \( \langle T \rangle + \langle V \rangle \), is half the separate errors in \( \langle T \rangle \) and \( \langle V \rangle \). In fact, \( \langle T \rangle + \langle V \rangle \) is seen to be systematically closer to the exact energy than the estimate \( \langle V_0 \rangle + \langle V \rangle/2 \) obtained from the virial theorem by elimination of the kinetic energy.
Table 3: Estimates of the hydrogen ground state energy. All values tabulated are in eV. The quantity $\Delta = \langle T \rangle - \langle V \rangle / 2$ should be zero, by the virial theorem. The last two columns should be compared to the exact value of $-13.598$ eV. See comments in the text.

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**A Example: Quadratic Lagrangian**

In the case of a particle of electric charge $q$ moving in an electromagnetic vector potential $A(r)$, the imaginary time action has also an imaginary part,

$$S = \int_0^{\beta \hbar} d\tau \left( \frac{1}{2} m (\dot{r}(\tau))^2 + V(r(\tau)) + i q \dot{r}(\tau) \cdot A(r(\tau)) \right).$$

Note that the contribution from the vector potential is gauge invariant, because we integrate over a closed path. The partition function can be computed exactly by the path integral for example when we have an isotropic harmonic oscillator external potential of angular frequency $\omega$, and a magnetic field of constant flux density $B$, so that

$$V(r) = \frac{1}{2} m \omega^2 r^2, \quad A(r) = \frac{B \times r}{2}.$$  \hspace{1cm} (85)

Then

$$\frac{S}{\hbar} = \beta m \omega^2 |a_0|^2 + \sum_{n=1}^{\infty} \left( C_n^2 + \beta m \omega^2 \right) |a_n|^2 + \frac{2 n \pi q}{\hbar} B \cdot (a_n \times a_n^*) \Bigg).$$  \hspace{1cm} (86)
and the partition function is, with $B = |B|$,

$$
Z = \frac{1}{(\beta \hbar \omega)^3} \prod_{n=1}^{\infty} \left[ \left( 1 + \left( \frac{\beta \hbar \omega}{2n\pi} \right)^2 \right) \left( 1 + \left( \frac{\beta \hbar \omega}{2n\pi} \right)^2 + \left( \frac{\beta \hbar |B|}{2n\pi m} \right)^2 \right) \right]^{-1}.
$$

(87)

The energy spectrum is of course well known. An energy eigenvalue is given by quantum numbers $j, k, \ell = 0, 1, 2, \ldots$ as

$$
E_{j,k,\ell} = \left( j + \frac{1}{2} \right) \hbar \omega_+ + \left( k + \frac{1}{2} \right) \hbar \omega_- + \left( \ell + \frac{1}{2} \right) \hbar \omega,
$$

(88)

where

$$
\omega_\pm = \sqrt{\omega^2 + \left( \frac{|qB|}{2m} \right)^2} \pm \frac{|qB|}{2m}.
$$

(89)

Hence,

$$
Z = \sum_{j,k,\ell} e^{-\beta E_{j,k,\ell}} = \frac{1}{8 \sinh \left( \frac{3 \hbar \omega_+}{2} \right) \sinh \left( \frac{3 \hbar \omega_-}{2} \right) \sinh \left( \frac{3 \hbar \omega}{2} \right)}.
$$

(90)

Equation (87) gives a product representation of this function.
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