



# Computation of the high temperature Coulomb density matrix in periodic boundary conditions



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## ABSTRACT

The high temperature many-body density matrix is fundamental to path integral computation. The pair approximation, where the interaction part is written as a product of pair density matrices, is commonly used and is accurate to order  $\tau^2$ , where  $\tau$  is the step size in the imaginary time. Here we present a method for systems with Coulomb interactions in periodic boundary conditions that consistently treats the all interactions with the same level of accuracy. It is shown that this leads to a more accurate high temperature solution of the Bloch equation. The method is applied to many-body simulation and tests for the isolated hydrogen atom and molecule are presented.

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## 1. Introduction

Quantum Monte Carlo (QMC) methods are frequently used to study interacting many-body systems in different fields of physics and chemistry when a high degree of accuracy is needed [1]. The description of correlation effects combined with favorable scaling properties of  $N^3$  or better ( $N$  is the number of particles) makes these techniques effective in many applications. Path integral Monte Carlo (PIMC) is unique among other QMC methods because it can describe quantum systems at *finite temperature* [2–6]. The method is based on the thermal density matrix that characterizes the properties of a system in thermal equilibrium. PIMC is a very efficient method to study dense plasmas [7–15] where electrons are partially excited because of the high temperature.

Many applications of the PIMC method require an accurate treatment of Coulomb interactions in periodic boundary conditions (PBC). This includes all electronic structure simulations that describe electrons as individual particles. However, there is still no universally accepted method to compute the Coulomb propagator in PBC, which has led to unnecessary approximations resulting in less efficient and less accurate many-body simulations.

In this article, we describe an accurate approach to compute the Coulomb pair density matrix in a periodic system. It can easily be generalized to other long range interactions [16]. The density matrix of a bosonic (B) or fermionic (F) system at temperature  $T$

can be expressed in terms of an imaginary-time path integral,

$$\rho_{B/F}(\mathbf{R}, \mathbf{R}'; \beta) = \frac{1}{N!} \sum_{\mathcal{P}} (\pm 1)^{\mathcal{P}} \times \int_{\mathbf{R} \rightarrow \mathcal{P}\mathbf{R}'} d\mathbf{R}_i \rho(\mathbf{R}, \mathbf{R}_1; \tau) \rho(\mathbf{R}_1, \mathbf{R}_2; \tau) \dots \rho(\mathbf{R}_{M-1}, \mathcal{P}\mathbf{R}'; \tau), \quad (1)$$

where  $\tau$  is the time step  $\tau = \beta/M$  with  $\beta = 1/k_B T$ , and  $k_B$  is Boltzmann's constant.  $N$  particles in real-space representation,  $\mathbf{R} = \{\mathbf{r}_1, \dots, \mathbf{r}_N\}$ , are described in the canonical ensemble. The sum over  $\mathcal{P}$  presents all possible permutations of identical particles. In the fermionic case, odd permutations enter with a negative weight. Atomic units of Bohr radii and Hartree will be used throughout this work.

Instead of employing the propagator at temperature,  $T$ , path integrals rely on a density matrix at much higher temperature,  $M \times T$ . At high temperature, the many-body density matrix can be computed with good accuracy because exchange effects as well as three-body correlations are negligible in this limit. A novel method of constructing the high temperature density matrix (HTDM) for systems with *long-range interactions with periodic boundary conditions* is the focus of this study.

Different approximations for the Coulomb HTDM have been advanced that all become exact in the limit of  $\tau \rightarrow 0$ . However, all PIMC simulations are performed at finite  $\tau$ . Therefore an accurate representation of the HTDM is very important since its accuracy determines the maximum time step  $\tau$  one can use. A larger time step allows one to significantly cut down on the number of time slices,  $M$ , in the path integral and therefore to improve the

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efficiency of many-body simulations. Such a efficiency gain may be crucial in practical applications in order to perform accurate simulations at low temperature or of large systems.

The HTDM can be used to define the potential action,  $U(\mathbf{R}, \mathbf{R}'; \tau)$ . For a system of  $N$  distinguishable particles in real space representation this reads,

$$\rho(\mathbf{R}, \mathbf{R}'; \tau) = \exp\{-U(\mathbf{R}, \mathbf{R}'; \tau)\} \prod_{i=1}^N \rho_0(\mathbf{r}_i, \mathbf{r}'_i; \tau). \quad (2)$$

$\rho_0$  is the free particle density matrix in  $D$  dimensions,

$$\rho_0(\mathbf{r}, \mathbf{r}'; \tau) = (4\pi\lambda\tau)^{-D/2} \exp\{-|\mathbf{r} - \mathbf{r}'|^2/4\lambda\tau\}. \quad (3)$$

$\lambda$  is a mass dependent parameter,  $\hbar^2/2m$ .  $U$  is commonly approximated as the product over the nonideal parts of all pair density matrices  $\rho(\mathbf{r}_{ij}, \mathbf{r}'_{ij}; \tau)$ ,

$$\begin{aligned} \exp\{-U(\mathbf{R}, \mathbf{R}'; \tau)\} &\approx \exp\left\{-\sum_{i<j} u(\mathbf{r}_{ij}, \mathbf{r}'_{ij}; \tau)\right\} \\ &= \prod_{i<j} \frac{\rho(\mathbf{r}_{ij}, \mathbf{r}'_{ij}; \tau)}{\rho_0(\mathbf{r}_{ij}, \mathbf{r}'_{ij}; \tau)}. \end{aligned} \quad (4)$$

This is called the *pair approximation*, and is accurate to order  $\tau^2$  [4–6]. One essentially starts with a exact solution of the two-body problem when performing many-body simulations. This means only one time slice is needed to simulate the hydrogen atom at any temperature but more slices are needed for the hydrogen molecule because in this case, three-body correlations are important. Exchange effects have been neglected in Eq. (4), which is well justified for small time steps,  $\tau$ . In the full path integral, Eq. (1), are included however because of the sum over permutations.

For a Coulomb system with periodic boundary conditions, these pair density matrices,  $\rho(\mathbf{r}, \mathbf{r}'; \tau)$ , are solutions of the two particle Bloch equation with the Ewald potential [17],

$$\frac{\partial \rho}{\partial \tau} = -\hat{H}\rho = \lambda_{ij} \nabla_{\mathbf{r}}^2 \rho - V_{EW}(\mathbf{r})\rho, \quad (5)$$

with the initial condition  $\rho(\mathbf{r}, \mathbf{r}'; \tau = 0) = \delta(\mathbf{r} - \mathbf{r}')$ . The reduced mass  $\mu_{ij} = m_i m_j / (m_i + m_j)$  enters through  $\lambda_{ij} \equiv \hbar^2/2\mu_{ij}$ . The pair density matrix can also be derived from the Feynman–Kac relation,

$$\rho(\mathbf{r}, \mathbf{r}'; \tau) = \rho_0(\mathbf{r}, \mathbf{r}'; \tau) \left\langle e^{-\int_0^\tau dt V(\mathbf{r}(t))} \right\rangle_{\mathbf{r} \rightarrow \mathbf{r}'}, \quad (6)$$

where the average is to be taken over all free-particle (Brownian) paths from  $\mathbf{r}$  to  $\mathbf{r}'$ . For potentials without negative singularities, this expression can easily be evaluated numerically for specific pairs of  $\mathbf{r}$  and  $\mathbf{r}'$ , which enables one to verify the approximations in the computation of the pair density matrix that we will introduce below. However, the results of Feynman–Kac calculations always have a statistical uncertainty due to the finite sample of Brownian paths.

The resulting Ewald pair action,  $u_{EW}(\mathbf{r}, \mathbf{r}'; \tau) = -\ln[\rho_{EW}/\rho_0]$ , determines the weight of the paths in Eq. (1) where  $\mathbf{r}$  and  $\mathbf{r}'$  represent the separations of pairs of particles  $i$  and  $j$  at two adjacent time slices at  $t$  and  $t + \tau$ ,

$$\mathbf{r} = \mathbf{r}_i(t) - \mathbf{r}_j(t), \quad \mathbf{r}' = \mathbf{r}_i(t + \tau) - \mathbf{r}_j(t + \tau). \quad (7)$$

For a spherically symmetric potential, the pair density matrix depends on  $\tau$  and three spatial variables: the initial and final pair separations  $|\mathbf{r}|$  and  $|\mathbf{r}'|$  as well as the angle between them  $\theta$ . Alternatively, it can be expressed in terms of the variables  $q, s$  and  $z$ ,

$$q \equiv \frac{1}{2}(|\mathbf{r}| + |\mathbf{r}'|), \quad s \equiv |\mathbf{r} - \mathbf{r}'|, \quad z \equiv |\mathbf{r}| - |\mathbf{r}'|. \quad (8)$$

For the Coulomb potential, the dependence on  $z$  drops out [18]. The Ewald potential, however, has the symmetry of the periodic simulation cell which requires both the initial and final pair separation to be specified with respect to the cell. This implies that the pair density matrix for the Ewald potential depends on six spatial variables. This makes computation and storage of the corresponding action extremely awkward.

Previous methods [19,20] to deal with this difficulty have involved a break-up of the Ewald potential into a spherically symmetric short-range piece and a long-range remainder,

$$V_{EW}(\mathbf{r}) = V_{s.r.}(|\mathbf{r}|) + V_{l.r.}(\mathbf{r}). \quad (9)$$

The short-range piece has been treated numerically using the matrix squaring technique developed by Storer [21]. In principle, it allows one to derive the exact action for a spherically symmetric potential but in practice the accuracy is controlled by numerical accuracy of the integration. Matrix squaring is performed on a grid and controlling the associated grid errors requires significant care [22]. To treat the cusp condition at the origin accurately, the short-range part must include the singular part of the potential. Most simply, one can use the direct  $1/r$  interaction term as short-range part. Alternatively, one can employ the optimized Ewald break-up method described in [23,24], which allows one to construct a short-range piece that always decays within the boundaries of the simulation cell. A detailed review of the break-up method and its accuracy is given in [22]. The *primitive approximation*,

$$u_{p.A.}(\mathbf{r}, \mathbf{r}'; \tau) = \frac{\tau}{2} [V(\mathbf{r}) + V(\mathbf{r}')], \quad (10)$$

provides a simple straightforward way to add the long-range remainder,

$$u(\mathbf{r}, \mathbf{r}'; \tau) \approx u_{s.r.}(\mathbf{r}, \mathbf{r}'; \tau) + \frac{\tau}{2} [V_{l.r.}(\mathbf{r}) + V_{l.r.}(\mathbf{r}')]. \quad (11)$$

but the random phase approximation has also been applied to the long-range action [20]. When we later refer to Eqs. (9) and (11), we assume that the  $1/r$  potential has been used as short-range piece.

The break-up of the Ewald potential [19,20] introduces an additional approximation to path integral computation. While it has been successful in many applications [25–28] there is a need for improvement. The break-up is *ad hoc* and introduces some arbitrariness to the construction of the Ewald action. The accuracy remains high if either potential piece is sufficiently smooth on the scale of the thermal de Broglie wave length,  $\lambda_d = \sqrt{4\pi\lambda\tau}$ . However, the convergence to the correct answer as function of cell size and temperature is difficult to assess. For these reasons, we present a method here that consistently treats the direct Coulomb interaction within the simulation cell and that with periodic images with the same level of accuracy. Our method thereby avoids introducing a short and long-range potential. The necessary pair density matrices are derived for the Coulomb potential, which makes it possible to utilize the large amount of analytic and numerical work available for this potential. The development of the method proceeds in steps that we will now describe.

## 2. Method

### 2.1. Computation of the pair density matrix for the coulomb potential

It is first necessary to compute the pair density matrix for an isolated pair of particles. This can either be done with matrix squaring or from the sum over eigenstates. In the matrix squaring technique, one can take advantage of the fact that only  $s$ -wave contributions enter in case of the Coulomb potential as done by Storer [21]. When using the squaring technique, one starts from

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