Path Integral Density Functional Theory

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Abstract

A new method (PI-DFT) which combines path integrals and density functional theory is proposed as a pathway to many fields of physics. Within path integral theory it is possible to construct particle densities without explicitly calculating individual wave functions. These densities can directly be used as an input to energy density functionals. Thus our method makes full use of the theorem of Hohenberg, Kohn and Sham which shows, that the energy of a many electron system only depends on the particle density.

At glance we present a recursion formula for the calculation of many fermion and boson particle densities from one-particle densities at a set of different temperatures. For both statistics the numerical effort of our method increases only with the square of the particle number.
Path integrals and Density Functional Theory have both been investigated and developed extensively in the past decades\(^1\). Here we present a new method (PI-DFT), which formally joins both fields and for the first time uses the theorem of Hohenberg, Kohn and Sham \([3,4]\) to its full extent. While the method is applicable to bosons as well, the most interesting case is that of fermions because of its great relevance in quantum chemistry. The pride of our method is that we never deal with individual wave functions to compute the particle densities but still solve the full problem. The basic underlying idea is a self-consistent iteration scheme, in which the particle density is computed by means of path integrals, while effective potentials and observables are computed with methods lent from density functional theory. For the problem of constructing completely antisymmetric or symmetric particle densities we propose a recursion formula which has originally been invented by us for the partition function \([5]\). With this formula there is no need to know the individual wave functions to construct the appropriate particle densities for Fermi-Dirac (FD) or Bose-Einstein (BE) statistics. Instead, these are calculated from single-particle densities but at different temperatures.

Using this formula the numerical effort for both statistics grows only with the square of the particle number.

In the following we will consider N-particle hamiltonians of the form

$$H = -\frac{\hbar^2}{2m} \sum_{i=1}^{N} \frac{d^2}{d\vec{x}_i^2} + \sum_{i=1}^{N} v(\vec{x}_i) + \sum_{k<l}^{N} u(|\vec{x}_k - \vec{x}_l|).$$\(^1\) (1)

That is, we assume the potential to contain one and two particle interaction terms as encountered typically in quantum chemical problems.

In conventional Path Integral Monte Carlo techniques for fermion systems an \(NM\) dimensional integral with an integrand containing an \((N \times N)\) determinant has to be calculated (see e.g. \([6,7]\)) resulting in a numerical effort proportional to \(N^4\). Equation (2) can be de-

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\(^1\)See for example \([6,7]\) and references therein.
A Trotter formula [8] can be derived easily using the Trotter formula and is equivalent to the thermal Path Integral as the number of time slices \( M \) goes to infinity.

\[
Z = \left( \frac{1}{N!} \right)^M \int \prod_{k=1}^{N} \prod_{\mu=1}^{M} d\vec{x}_k(\mu) \left\{ \prod_{\nu=1}^{M} \det A(\nu) \times \exp \left( -\frac{\beta}{M} \left[ \sum_{k=1}^{N} v(\vec{x}_k(\nu)) + \sum_{k<l}^{N} u(|\vec{x}_k(\nu) - \vec{x}_l(\nu)|) \right] \right) \right\}
\]

with

\[
(A(\mu))_{k,l} = \left( \frac{Mm}{2\pi\beta\hbar^2} \right)^{3/2} \exp \left( -\frac{Mm}{2\beta\hbar^2} (\vec{x}_k(\mu) - \vec{x}_l(\mu + 1))^2 \right),
\]

\( \vec{x}_k(M + 1) \equiv \vec{x}_k(1) \).

Although the method is suitable for systems like \(^3\)He clusters [9] and most physical relevant observables can be calculated, its application is numerically very extensive in general.

According to the theorem of Hohenberg, Kohn and Sham [3,4] and its extension to thermal systems given by Mermin [10] the potential given by the term in square brackets in (2) can be replaced by an effective one-particle potential.

\[
\varphi(\vec{x}) = v(\vec{x}) + \int d\vec{x}' \eta(\vec{x}') u(|\vec{x}' - \vec{x}|).
\]

Since the energy is only a functional of the one particle density \( \eta(\vec{x}) \), which can be easily calculated within the approximation (2) by Monte Carlo methods and \( \varphi(\vec{x}) \), the solution of the stated problem, can be found by self-consistent iteration of (2) and (3). A priori the use of this approximation has no advantages compared to the direct calculation of (2), but together with a much more effective way of calculating the partition function, which will be stated in the following, the above iteration scheme develops to a very powerful tool.

Let us denote with \( \eta_N(\vec{x}; \beta) \) the probability of finding a particle at position \( \vec{x} \) in a system of \( N \) noninteracting fermions or bosons moving in a common potential thermalized at temperature \( \beta \) and with \( Z_N(\beta) \) the corresponding canonical partition function. For such a system it is sufficient to compute the one-particle densities \( \eta_i(\vec{x}; \beta), \eta_i(\vec{x}; 2\beta), \ldots, \eta_i(\vec{x}; N\beta) \),
but at a set of different temperatures. Then $Z_N(\beta)$ and $\eta_N(\vec{x}, \beta)$ can be calculated by the recursion formulas

$$Z_N(\beta) = \frac{1}{N} \sum_{k=1}^{N} (\pm)^{k+1} Z_1(k\beta) Z_{N-k}(\beta)$$  \hspace{1cm} (4)$$

$$\eta_N(\vec{x}; \beta) = Z_{N-1}^{-1}(\beta) \sum_{k=1}^{N} (\pm)^{k+1} Z_1(k\beta) \eta_1(\vec{x}, k\beta) Z_{N-k}(\beta)$$  \hspace{1cm} (5)$$

where the plus and the minus signs stand for Fermi-Dirac and Bose-Einstein statistics, respectively, and $Z_0(\beta) \equiv 1$.

The proof for (4) has already been given explicitly in [5]. The validity of (5) can be proven in the same manner. As the whole procedure is somewhat lengthy, we omit it here and sketch the basic idea using the two-fermion system as an example.

Let $\epsilon_k$ denote the energy eigenvalues of the one-particle system and $\psi_k$ the corresponding eigenfunctions. Then the partition function is given by

$$Z_2(\beta) = \frac{1}{2} \sum_k \sum_{l \neq k} \exp(-\beta(\epsilon_k + \epsilon_l)) .$$  \hspace{1cm} (6)$$

The probability $p_k$ of finding a particle in the one-particle state $| k \rangle$ is simply

$$p_k = Z_2^{-1}(\beta) \frac{1}{2} \sum_{l \neq k} \exp(-\beta(\epsilon_k + \epsilon_l))$$  \hspace{1cm} (7)$$

$$= Z_2^{-1}(\beta) \frac{1}{2} \sum_l \exp(-\beta(\epsilon_k + \epsilon_l)) - \exp(-2\beta\epsilon_k)$$

$$= Z_2^{-1}(\beta) \frac{1}{2} [\exp(-\beta\epsilon_k) Z_1(\beta) - \exp(-2\beta\epsilon_k)]$$

For the particle density this yields

$$\eta_2(\vec{x}; \beta) = \sum_k p_k | \psi_k(\vec{x}) |^2$$  \hspace{1cm} (8)$$

$$= Z_2^{-1}(\beta) \sum_k | \psi_k(\vec{x}) |^2 [\exp(-\beta\epsilon_k) Z_1(\beta) - \exp(-2\beta\epsilon_k)]$$

$$= Z_2^{-1}(\beta) \left[ Z_1^2(\beta) \eta_1(\vec{x}; \beta) - Z_1(2\beta) \eta_1(\vec{x}; 2\beta) \right] ,$$

which is nothing but equation (5) for the special case $N = 2$.

A simple example shows that the given formulas work very well and exactly. We calculated the exact solvable system of $N$ uncoupled harmonic oscillators.
for both statistics. The one particle densities $\eta_i(\vec{x}; k\beta)$ shown in Fig. 1 are calculated with standard path integral techniques (see e.g. [6,7]). In Fig. 2 and Fig. 3 the exact particle densities and the densities calculated via (3) are shown for both statistics. The outcome is an almost perfect agreement with the exact results. The computed energies agree equally well with the exact values. For our examples the errors were in all cases below 0.1 %.

Obviously it is essential in the fermion case, that there is a nonvanishing occupation probability of the excited states for the chosen temperature, i.e. the results of the one-particle Path Integral Monte Carlo simulations have to contain information about the excited states. Because of the fact that in the low temperature range the energy is in general a very slowly increasing function in the case of Fermi-Dirac statistics, this is not a too bad restriction, even if one is going to calculate ground state properties of the fermion system.

Possibly the most interesting topic concerning PI-DFT is an analysis of its computational costs. The basic steps in PI-DFT are the following:

1. Construction of an initial guess for the N particle density.
2. Calculation of the effective potential.
3. Calculation of single-particle densities and the corresponding energies at N different temperatures.
4. Calculation of the partition function by spline interpolation of the caloric curve along with numerical integration using

$$Z(\beta) = \exp(-\int_{\beta_0}^{\beta} d\beta' E(\beta') + F_0).$$ \hspace{1cm} (10)

5. Calculation of the N-particle partition function using (4).
6. Calculation of the N-particle density using (5).
Steps 2-6 have to be repeated until the particle densities and the energy are converged. The main numerical effort lies in the steps 2 and 3. The calculation of the effective potential is usually proportional to $N^2$. Because of the fact that the numerical effort of a Path Integral Monte Carlo simulation grows normally proportionally to $\beta$ the same applies to step 3. Steps 4 and 5 are negligible, while the effort for step 6 again grows proportionally to $N^2$ assuming that the number of used grid points is approximately proportional to the number of particles. Overall this indeed yields a numerical effort proportional to the square of the particle number for PI-DFT. Hence it follows that PI-DFT can be seen as a formal proof, that e.g. quantum chemical calculations can be done with such a slowly increasing numerical effort. We hope that this will encourage further improvements of other related methods, too. This paper presents only the onset of PI-DFT and a lot of improvements seem to be possible and required. For example, the recursion for the partition function might be numerically unstable under unfavorable circumstances in the case of FD statistics because of the alternating sums.

In a forthcoming paper we will present a study on $^4$He clusters as a first physical application of PI-DFT.

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FIGURES

FIG. 1. Particle densities $\eta_1(\vec{x}; \beta)$ calculated with Path Integral Monte Carlo for various temperatures ($\hbar = k = m = 1$).

FIG. 2. Exact harmonic oscillator particle densities and particle densities calculated with Path Integral Monte Carlo in connection with equation (3) for $N=2$ at $T=0.5$ and $N=4$ at $T=2.0$ for the case of FD statistics ($\hbar = k = m = 1$).

FIG. 3. Exact harmonic oscillator particle densities and particle densities calculated with Path Integral Monte Carlo in connection with equation (3) for $n=2$ at $T=0.5$ and $N=4$ at $T=1.0$ for the case of BE statistics ($\hbar = k = m = 1$).
$|\phi|^2$ vs $X$

- $N=4$, $T=2.0$ (exact)
- $N=4$, $T=2.0$ (PI-DFT)
- $N=2$, $T=0.5$ (exact)
- $N=2$, $T=0.5$ (PI-DFT)
$\phi^2$

- $N=4$, $T=1.0$ (exact)
- $N=4$, $T=1.0$ (PI-DFT)
- $N=2$, $T=0.5$ (exact)
- $N=2$, $T=0.5$ (PI-DFT)