Nonzero-temperature path-integral method for fermions and bosons: A grand canonical approach

M. Skorobogatiy and J. D. Joannopoulos
Department of Physics, MIT, Cambridge, Massachusetts 02139
(Received 6 July 1998; revised manuscript received 8 December 1998)

The calculation of the density matrix for fermions and bosons in the grand canonical ensemble allows an efficient way for the inclusion of fermionic and bosonic statistics at all temperatures. It is shown that in a path-integral formulation the one-particle density matrix can be expressed via an integration over a novel representation of the universal temperature-dependent functional. In this paper we discuss a representation for the universal functional in terms of Hankel functions which is convenient for computational applications. Temperature scaling for the universal functional and its derivatives is also introduced thus allowing an efficient rescaling rather then recalculation of the functional at different temperatures. We expect that our method will give rise to a numerically efficient path-integral approach for calculation of a density matrix in the grand canonical ensemble. [S0163-1829(99)06127-5]

I. INTRODUCTION

In fermionic systems, the problem of interacting electrons can be treated effectively in the Kohn Sham (KS) density-functional formalism.[1] According to KS a problem of N interacting fermions with a Hamiltonian H_0 can be mapped into a problem of N noninteracting particles described by a modified Hamiltonian H, which is, in turn, a functional of the density (see the review[2])

$$H=T(\rho)+V_{ion}(r)+V_H(r)+V_{XC}(r), \tag{1}$$

where $T(\rho)$ is a kinetic-energy functional, $V_{ion}(r)$ is an electron-ion interaction potential, $V_H(r)$ is the Hartree potential

$$V_H(r)=e^2\int\frac{\rho(r',r';\beta,\mu)}{|r-r'|}d^3r', \tag{2}$$

and $V_{XC}(r)$ is a universal exchange-correlation electron density functional given by

$$V_{XC}(r)=\frac{\delta E_{XC}[\rho(r,r;\beta,\mu)]}{\delta\rho(r,r;\beta,\mu)}. \tag{3}$$

The temperature-dependent fermion density matrix is defined as

$$\rho(r,r';\beta,\mu)=\langle r|\frac{1}{Z^{-1}\exp(\beta H)+1}|r'\rangle. \tag{4}$$

For noninteracting particles, a self-consistent algorithm for finding the density matrix in the grand canonical formulation is typically:

(a) Use $\rho(r,r;\beta,\mu)$ to find a new effective Hamiltonian H.

(b) Given H calculate a new $\rho(r,r;\beta,\mu)$ from

$$\rho(r,r';\beta,\mu)=\langle r|\frac{1}{Z^{-1}\exp(\beta H)+1}|r'\rangle. \tag{5}$$

(c) Update the chemical potential μ [which comes via $Z=\exp(\beta\mu)$].

(d) If self-consistency is not achieved go to (a).

Up to this point the algorithm is rather general and can be implemented in many ways. One of the implementations of this algorithm for fermions is originally due to Goedecker[3] and lately extended by Baer.[4] The most important step involves implementation of part (b). For example,

$$\rho(r,r';\beta,\mu)=\langle r|\frac{1}{Z^{-1}\exp(\beta H)+1}|r'\rangle$$
$$=\sum_{k=1}^{\infty}\sum_{k'=1}^{\infty}\langle r|k\rangle\langle k|\frac{1}{Z^{-1}\exp(\beta H)+1}|k'\rangle$$
$$\times\langle k'|r'\rangle, \tag{6}$$

where $\langle r|k\rangle$ is any convenient basis set. By approximating $1/[Z^{-1}\exp(\beta H)+1]=\mathrm{Pol}(H;\beta)$ using Chebyshev polynomials, Goedecker *et al.* obtained an efficient way of calculating the density matrix using $\mathrm{Pol}(H;\beta)$ as a propagator.

An alternative and potentially beneficial method for implementation of step (b) is to use the path-integral approach.[5,6] It will be shown in Sec. II that the density matrix for fermions and bosons can be presented as

$$\rho(r,r';\beta,\mu)\sim\lim_{P\to\infty}\int dL_P^2dK_{Po}^2D(L_P^2,K_{Po}^2)$$
$$\times F_{bos,ferm}(\beta,P,L_P^2,\mu+K_{Po}^2), \tag{7}$$

where, briefly, $F_{bos,ferm}(\beta,P,L_P^2,K_{Po}^2)$ is a universal functional of variables K_{Po}^2 and L_P^2, and $D(L_P^2,K_{Po}^2)$ is a nonuniversal system-dependent probability distribution of these variables. Thus, one can precalculate the universal functional

and employ Monte Carlo techniques to calculate a distribution of K_{Po}^2 and L_P^2 for any particular system. Since the computational effort mostly involves a calculation of a two-dimensional (2D) nonuniversal probability distribution $D(L_P^2, K_{Po}^2)$ this method may prove to be advantageous for computational purposes due to the functional simplicity of the variables K_{Po}^2 and L_P^2.

Below, we confine ourselves to a derivation and discussion of this universal functional and the important scaling laws associated with it. Although we are primarily interested in fermions we also include wherever possible the derivation for bosons as well.

II. ALL TEMPERATURE SOLUTION

In the path-integral formalism, evaluation of the density matrix for fermions or bosons proceeds by inserting P auxiliary states between position operators thereby reducing the problem to the evaluation of $\langle r|(1/\{\exp[\beta(H-\mu)] \pm 1\})^{1/P}|r'\rangle$.[7–9] At high temperatures the conventional use of the Trotter approximation for separating kinetic and potential energy contributions is applicable and one obtains

$$\begin{aligned}\langle r|\left(\frac{1}{\exp[\beta(H-\mu)]\pm 1}\right)^{1/P}|r'\rangle &\sim \langle r|\exp\left(-\frac{\beta}{P}(H-\mu)\right)|r'\rangle \\ &\sim \langle r|\exp\left(-\frac{\beta}{P}T_{kin}\right)|r'\rangle\exp\left(-\frac{\beta}{P}V(r')\right). \quad (8)\end{aligned}$$

At low temperatures $\beta\to\infty$ and, in the case of fermion statistics,

$$\langle rf|\left(\frac{1}{\exp[\beta(H-\mu)]\pm 1}\right)^{1/P}|r'\rangle \sim \theta(\mu-H), \quad (9)$$

where $\theta(x)$ is a step function and the propagator becomes invariant with respect to P. Thus, for large P, the propagator $\langle r|\{1/\exp[\beta(H-\mu)]\pm 1\}^{1/P}|r'\rangle$ is easy to estimate at high temperatures while at low temperatures it becomes P independent, requiring new methods to be developed.

The problem of evaluation of the fermionic density matrix at zero temperature can be solved exactly in the path-integral formulation in terms of Bessel functions.[8] For the case of nonzero temperatures the problem has also been solved with the fermionic density matrix represented in integral form.[9] However, there exists a more computationally convenient representation for the fermionic and bosonic density matrix in terms of the Hankel functions of the first kind.

To calculate the density matrix in the grand canonical ensemble, we exploit the property of a meromorphic function being equal to a summation over its poles and residues. Thus

$$\frac{1}{\exp[\beta(H-\mu)]\pm 1} = \pm\frac{1}{2} \pm \sum_{n=-\infty}^{+\infty} \frac{1}{iw_n-\beta(H-\mu)}, \quad (10)$$

where $w_n=\pi(2n+1)$ for fermions and $w_n=2\pi n$ for bosons. The density matrix now can be written as

$$\begin{aligned}&\langle r|\frac{1}{\exp[\beta(H-\mu)]\pm 1}|r'\rangle \\ &\quad = \pm\frac{\delta(r-r')}{2} \pm \sum_{n=-\infty}^{+\infty}\langle r|\frac{1}{iw_n-\beta(H-\mu)}|r'\rangle. \quad (11)\end{aligned}$$

In this form it is still difficult to make a transition to a path-integral formalism. We notice, however, that for $w_n>0$

$$\frac{1}{iw_n-\beta(H-\mu)} = -i\int_0^{+\infty} dt\,\exp[-tw_n-it\beta(H-\mu)] \quad (12)$$

and for $-w_n$

$$\frac{1}{-iw_n-\beta(H-\mu)} = i\int_0^{+\infty} dt\,\exp[-tw_n+it\beta(H-\mu)]. \quad (13)$$

Thus, evaluation of $\langle r|1/[iw_n-\beta(H-\mu)]|r'\rangle$ is now substantially simplified and we can change to a path-integral formulation with

$$\begin{aligned}&\langle r|\frac{1}{iw_n-\beta(H-\mu)}|r'\rangle \\ &\quad = -i\int_0^{+\infty} dt\,\exp(-tw_n)\langle r|\exp[-it\beta(H-\mu)]|r'\rangle. \quad (14)\end{aligned}$$

The matrix element $\langle r|\exp[-it\beta(H-\mu)]|r'\rangle$ is nothing else but a real-time propagator. Its evaluation in a path-integral formalism is trivial and leads to

$$\begin{aligned}&\langle r|\exp[-it\beta(H-\mu)]|r'\rangle \\ &\quad = \lim_{P\to\infty}\left(\frac{-imP}{2\pi\hbar t\beta}\right)^{3P/2}\exp\left[i\left(\frac{ml_p^2}{2\hbar t}+\frac{\hbar k_p^2 t}{2m}\right)\right], \quad (15)\end{aligned}$$

where

$$\frac{\hbar^2 k_p^2}{2m} = \beta\left[\mu-\frac{1}{P}\left(\frac{V(\mathbf{r})+V(\mathbf{r}')}{2}+\sum_{i=1}^{P-1}V(\mathbf{r}^{(i)})\right)\right] \quad (16)$$

$$l_p^2=\frac{P}{\beta}\left((\mathbf{r}-\mathbf{r^{(1)}})^2+\sum_{i=1}^{P-2}(\mathbf{r^{(i)}}-\mathbf{r^{(i+1)}})^2+(\mathbf{r^{(P-1)}}-\mathbf{r}')^2\right). \tag{17}$$

Finally, for $w_n>0$

$$\langle r|\frac{1}{iw_n-\beta(H-\mu)}|r'\rangle = -i\int_{0-i\eta}^{+\infty-i\eta}dt\exp(-tw_n)\left(\frac{-imP}{2\pi\hbar t\beta}\right)^{3P/2} \times\exp\left[i\left(\frac{ml_p^2}{2\hbar t}+\frac{\hbar k_p^2 t}{2m}\right)\right] \tag{18}$$

and for $-w_n$

$$\langle r|\frac{1}{-iw_n-\beta(H-\mu)}|r'\rangle = i\int_{0+i\eta}^{+\infty+i\eta}dt\exp(-tw_n)\left(\frac{imP}{2\pi\hbar t\beta}\right)^{3P/2} \times\exp\left[-i\left(\frac{ml_p^2}{2\hbar t}+\frac{\hbar k_p^2 t}{2m}\right)\right]. \tag{19}$$

Using the integral representation of the Hankel functions[10]

$$H_n^{(1)}(z)=-\frac{i}{\pi}\exp\left(-\frac{1}{2}in\pi\right)z^n\int_0^{+\infty}\frac{dt}{t^{n+1}}\exp\left[\frac{1}{2}i\left(t+\frac{z^2}{t}\right)\right] \tag{20}$$

and summing over all frequencies, it is easy to show that the expression for the density matrix can be rewritten for fermions as

$$\rho(\mathbf{r},\mathbf{r}';\beta,\mu)=\frac{\delta(r-r')}{2}+\lim_{P\to\infty}\int d\mathbf{r^{3P}}F_{ferm}(\beta,P,L_P^2,K_P^2), \tag{21}$$

where

$$F_{ferm}(\beta,P,L_P^2,K_P^2) =\left(\frac{P}{2\pi}\right)^{3P/2}\mathrm{Re}\left[\left\{\frac{-2\pi i}{\beta}\sum_{n=0}^{\infty}\left(\frac{z_n}{L_P^2}\right)^{3P/2-1} \times H^{(1)}_{3P/2-1}(z_n)\right\}\right]. \tag{22}$$

For bosons

$$\rho(\mathbf{r},\mathbf{r}';\beta,\mu)=-\frac{\delta(r-r')}{2}-\lim_{P\to\infty}\int d\mathbf{r^{3P}} \times F_{bos}(\beta,P,L_P^2,K_P^2), \tag{23}$$

where

$$F_{bos}(\beta,P,L_P^2,K_P^2) =\left(\frac{P}{2\pi}\right)^{3P/2}\mathrm{Re}\left[\left\{\frac{-2\pi i}{\beta}\sum_{n=1}^{\infty}\left(\frac{z_n}{L_P^2}\right)^{3P/2-1} \times H^{(1)}_{3P/2-1}(z_n)\right\}+\lim_{w_0\to+0}\left\{\frac{-\pi i}{\beta}\left(\frac{z_0}{L_P^2}\right)^{3P/2-1} \times H^{(1)}_{3P/2-1}(z_0)\right\}\right] \tag{24}$$

and

$$z_n=\left[\left(K_P^2+i\frac{2w_n}{\beta}\right)L_P^2\right]^{1/2};\quad w_n^{ferm}=\pi(2n+1);$$

$$w_n^{bos}=2\pi n \tag{25}$$

$$\frac{\hbar^2K_P^2}{2m}=\mu-\frac{1}{P}\left(\frac{V(\mathbf{r})+V(\mathbf{r}')}{2}+\sum_{i=1}^{P-1}V(\mathbf{r^{(i)}})\right) \tag{26}$$

$$L_P^2=P\left((\mathbf{r}-\mathbf{r^{(1)}})^2+\sum_{i=1}^{P-2}(\mathbf{r^{(i)}}-\mathbf{r^{(i+1)}})^2+(\mathbf{r^{(P-1)}}-\mathbf{r}')^2\right). \tag{27}$$

In the case of bosons, term in the summation corresponding to zero frequency w_0 should be calculated in a limit $w_0\to+0$.

III. SCALING OF THE UNIVERSAL FUNCTIONAL

Above we showed that the density matrix for fermions and bosons can be expressed via a universal functional $F_{bos,ferm}(\beta,P,L_P^2,K_P^2)$ as

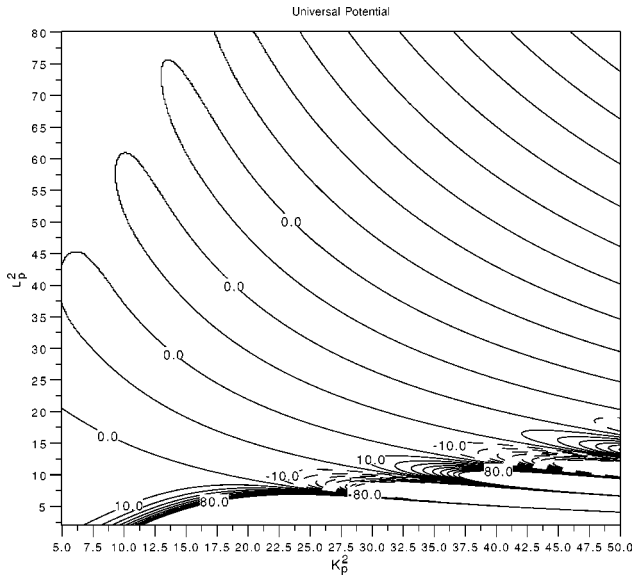

FIG. 1. $F_{ferm}(\beta=1.0,P=20,L_P^2,K_{Po}^2)$. Note the strong oscillations arising from the nature of fermionic statistics.

$$\rho(\mathbf{r},\mathbf{r}';\beta,\mu)=\pm\frac{\delta(r-r')}{2}\pm\lim_{P\to\infty}\int d\mathbf{r}^{3\mathbf{P}} \times F_{bos,ferm}(\beta,P,L_P^2,K_P^2). \quad (28)$$

From the explicit form of the universal functional derived above one can easily derive a scaling law

$$F_{bos,ferm}(\beta,P,L_P^2,K_P^2) = \beta^{-3P/2}F_{bos,ferm}(1,P,L_P^2\beta^{-1/2},K_P^2\beta^{1/2}). \quad (29)$$

This scaling law can be useful if we consider that the integral over the universal functional can be rewritten as

$$\int d\mathbf{r}^{3\mathbf{P}}F_{bos,ferm}(\beta,P,L_P^2,K_P^2) = \int dL_P^2 dK_{Po}^2 D(L_P^2,K_{Po}^2)F_{bos,ferm}(\beta,P,L_P^2,\mu+K_{Po}^2), \quad (30)$$

where

$$\frac{\hbar^2K_{Po}^2}{2m}=-\frac{1}{P}\left[\frac{V(\mathbf{r})+V(\mathbf{r}')}{2}+\sum_{i=1}^{P-1}V(\mathbf{r}^{(\mathbf{i})})\right] \quad (31)$$

and $D(L_P^2,K_{Po}^2)$ is the distribution of pairs of variables (L_P^2,K_{Po}^2). So, in principle, it is enough to calculate the universal functional once for say $\beta=1.0$ and the value of the functional at all other temperatures can be evaluated using the scaling law. For example, in Fig. 1 we show a plot of F_{ferm} for $\beta=1$ and $P=20$ as a function of L_P and K_{Po}. Note that as we vary temperature, this plot will simply expand and contract along the corresponding axes as dictated by Eq. (29).

The integration process in Eq. (30) could be implemented by first calculating the distribution $D(L_P^2,K_{Po}^2)$ (which actually depends upon $\mathbf{r}$ and $\mathbf{r}'$) and then multiplying this distribution on the values of the universal functional calculated on a 2D grid shifted by $-\mu$ along the K_{Po}^2 axis.

The averages and thermodynamic derivatives of the generic operator $U(\mathbf{r},\mathbf{r}')$ can now be determined from

$$\langle U(\mathbf{r},\mathbf{r}')\rangle_\beta=\int d\mathbf{r}d\mathbf{r}'\rho(\mathbf{r},\mathbf{r}';\beta,\mu)U(\mathbf{r},\mathbf{r}'), \quad (32)$$

and its derivatives from

$$\frac{\partial\langle U(\mathbf{r},\mathbf{r}')\rangle_\beta}{\partial\beta}=\int d\mathbf{r}d\mathbf{r}'\frac{\partial\rho(\mathbf{r},\mathbf{r}';\beta,\mu)}{\partial\beta}U(\mathbf{r},\mathbf{r}') \quad (33)$$

$$\frac{\partial\langle U(\mathbf{r},\mathbf{r}')\rangle_\beta}{\partial\mu}=\int d\mathbf{r}d\mathbf{r}'\frac{\partial\rho(\mathbf{r},\mathbf{r}';\beta,\mu)}{\partial\mu}U(\mathbf{r},\mathbf{r}'). \quad (34)$$

The thermodynamic derivatives of the density matrix can be calculated using the scaling relation for the universal functional giving

$$\frac{\partial\rho(\mathbf{r},\mathbf{r}';\beta,\mu)}{\partial\mu}=\lim_{P\to\infty}\pm\frac{1}{\beta^{(3P-1)/2}} \times\int dL_P^2dK_{Po}^2P(L_P^2,K_{Po}^2) \times\frac{\partial F_{bos,ferm}(1,P,L_P^2\beta^{-1/2},K_P^2\beta^{1/2})}{\partial K_P^2} \quad (35)$$

and

$$\frac{\partial\rho(\mathbf{r},\mathbf{r}';\beta,\mu)}{\partial\beta}=\lim_{P\to\infty}\pm\frac{1}{2\beta^{(3P+1)/2}}\int dL_P^2dK_{Po}^2P(L_P^2,K_{Po}^2) \times\left\{\frac{\partial F_{bos,ferm}(1,P,L_P^2\beta^{-1/2},K_P^2\beta^{1/2})}{\partial K_P^2} -\frac{1}{\beta}\frac{\partial F_{bos,ferm}(1,P,L_P^2\beta^{-1/2},K_P^2\beta^{1/2})}{\partial L_P^2} -\frac{3P}{\beta^{1/2}}F_{bos,ferm}(1,P,L_P^2\beta^{-1/2},K_P^2\beta^{1/2})\right\}. \quad (36)$$

IV. CONCLUSIONS

A grand canonical formulation of the path-integral formalism allows an effective treatment of the fermionic and bosonic systems. In this formulation the one-particle density matrix can be expressed as an integral over a universal functional $F_{bos,ferm}(\beta,P,L_P^2,K_{Po}^2)$ with the variables L_P^2, K_{Po}^2 being determined by the specific potential being used. A computationally convenient representation of the universal functional is possible in terms of Hankel functions of the first kind so one can, in principle, precalculate $F_{bos,ferm}(\beta,P,L_P^2,K_{Po}^2)$, and the density itself will be determined by a distribution of the nonuniversal variables L_P^2, K_{Po}^2. Due to the functional simplicity of the variables K_{Po}^2 and L_P^2, this method may prove to be advantageous for computational purposes.

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