OCT 26 1967

UCD-CNL 82
AEC RESEARCH &
DEVELOPMENT REPORT

CONF-670828--1

CROCKER NUCLEAR LABORATORY

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Density-Matrix Variational

Principles at Finite Temperatures

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August 14, 1967

Presented at the Density Matrix Conference

Queens University

Kingston, Ontario (1967)

There is no objection from the patent
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California Patent Group, USAEC

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Prepared Under October 24, 1967
Contract AT(11-1)-Gen 10, P. A. #15

for the
San Francisco Operations Office
U. S. Atomic Energy Commission

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Introduction.

Until very recently work done on variational principles involving reduced density matrices has been confined almost entirely to principles involving the ground-state properties of quantum systems. During the past year Kijewski and Percus¹ have attacked the problem of extending the density matrix variational methods to systems at non-zero temperature by using the free-energy minimum principle. The work presented in this paper is a somewhat different approach to the same problem.

Variational Principles at $T = 0$.

The density matrix D_N of an N -fermion (N -boson) system is an integral operator, on the space of functions of N variables, which has the following properties:

1. The eigenvalue spectrum of D_N is discrete and non-negative.
2. The trace of D_N is equal to one.
3. The eigenfunctions of D_N are all antisymmetric (symmetric).

Thus the kernel of D_N may be written in the form:

$$D_N(x_1, \dots, x_N | y_1, \dots, y_N) = \sum_n \lambda_n \psi_n(x_1, \dots, x_N) \psi_n^*(y_1, \dots, y_N) \quad (1)$$

where the functions ψ_N are orthonormal and antisymmetric (symmetric) and the eigenvalues λ_N satisfy the equations:

$$\lambda_n \geq 0 \quad \sum_n \lambda_n = 1. \quad (2)$$

¹L. J. Kijewski and J. K. Percus, *Lower Bounds to the Many-Body Problem Using Density Matrices*. (Courant Institute Preprint.)

Let us denote by the symbol $\mathcal{D}_N$ the class of all such integral operators. The two-particle reduced density matrix, or more simply the 2-matrix, is an integral operator on the space of functions of two variables whose kernel is obtained from that of D_N by contracting the last $N-2$ variables.

$$D_1(x_1, x_2 | y_1, y_2) = N(N-1) \int D_N(x_1, x_2, z_1, \dots, z_{N-2} | y_1, y_2, z_1, \dots, z_{N-2}) dz_1 \dots dz_{N-2}. \quad (3)$$

If we denote by $\mathcal{D}_2$ the class of all 2-matrices obtainable in this way from the operators in $\mathcal{D}_N$ then we can formulate the Rayleigh-Ritz variational principle in terms of the class $\mathcal{D}_2$.

$$E_0 = \min_{\mathcal{D}_2} \{ \text{Trace}(h D_2) \} \quad (4)$$

where Min means that the minimum is taken only with respect to operators $\mathcal{D}_2$.

The two-body Hamiltonian operator h is related to the Hamiltonian of the N -particle system in the following way:

$$H = \sum_{i \neq j} h(i, j) \quad (5)$$

In the most common case of a Hamiltonian which includes kinetic energy terms, an external potential $U(x)$, and interparticle interaction potentials $V(x_{ij})$ the operator h is given by:

$$h(1, 2) = \frac{1}{2(N-1)} \left[-\frac{\hbar^2}{2m} (\nabla_1^2 + \nabla_2^2) + U(x_1) + U(x_2) \right] + \frac{1}{2} V(x_{12}). \quad (6)$$

The problem of describing the class of operators $\mathcal{D}_2$ without making reference to $\mathcal{D}_N$ is a difficult one which has been studied for a number of years.^(2, 3)

² A. J. Coleman, Rev. Mod. Phys., 35, 658 (1963)

³ C. Garrod & J. K. Percus, J. Math. Phys. 5, 1756 (1964)
[Further references may be found in these papers.]

All of the partial solutions obtained to date may be described as various ways of constructing classes of two-particle operators which are guaranteed to contain $\mathcal{D}_2$. Given a class of integral operators Ω which contains $\mathcal{D}_2$ as a subset we have the following inequality:

$$E_0 \geq \min_{\Omega} \{ \text{Trace}(h D_2) \} \quad (7)$$

In this paper we shall consider extension of the above inequality to systems at non-zero temperature.

Variational Principles at $T \neq 0$.

The quantum mechanical form of the free-energy minimum principle states that the free energy, $F = E - TS$, of a system described by the Hamiltonian H is given by:

$$F = \min_{\mathcal{D}_N} \{ \text{Tr}(H D_N) + kT \text{Tr}(D_N \log D_N) \} \quad (8)$$

where the logarithm of the density matrix is defined in terms of the eigenvalues and eigenfunctions of D_N (see equations 1 and 2) by:

$$\log D_N = \sum_n (\log \lambda_n) \psi_n(x_1, \dots, x_N) \psi_n^*(y_1, \dots, y_N). \quad (9)$$

Any attempt to convert the above principle into a variational principle involving only one- and two-particle density matrices naturally runs into all the difficulties associated with the ground-state variational principle; namely the N -representability problem. However, there is now, besides the familiar difficulties, an unwelcome stranger; the two-particle entropy problem. The terms $\text{Tr}(D_N \log D_N)$ is not linear in D_N . Thus, even if we are sure that a particular 2-matrix $D_2(x_1, x_2 | y_1, y_2)$ is N -representable there is no obvious way of associating an entropy value with it. There is no reason to believe that the class of N -matrices which yield a given

2-matrix all have the same entropy. Since we are interested in minimizing the free energy the most natural way of choosing an N-matrix from that class would be to choose that one which yielded the largest entropy. Unfortunately any attempt to calculate the maximum entropy consistent with a given 2-matrix leads immediately to an N-particle statistical mechanics problem which is of exactly the same type and degree of difficulty as the one we hope to avoid by using reduced density matrices. Maximizing the entropy with a fixed 2-matrix is at least as difficult as maximizing the entropy with fixed energy. Since it is quite unlikely that any exact solution to the problem will be found we must consider the possibility of finding useful approximate solutions.

The approximate solutions to the entropy problem which we shall consider in this paper all involve the maximization of the entropy with constraints which are weaker than the constraint of fixed 2-matrix. In each case the entropy obtained is greater than the maximum entropy associated with the given 2-matrix. We thus obtain a free energy which is smaller than the true free energy.

If, instead of maximizing the entropy with the constraint that the 2-matrix remain fixed, we maximized it with the weaker constraint that the 1-matrix remain fixed then the mathematical problem encountered is an easily solvable one and we may obtain the maximum entropy consistent with a given 1-matrix in terms of the eigenvalues of the 1-matrix. If a_n and $a_n^\dagger$ are creation and destruction operators for the eigenfunctions of the 1-matrix then the 1-matrix has the form:

$$D_1(x|y) = \sum_n \bar{w}_n \phi_n(x) \phi_n^*(y) \quad (10)$$

where:

$$\bar{N}_n = \text{Tr}(a_n^\dagger a_n D_n) \quad (11)$$

If we want to minimize $\text{Tr}(D_n \log D_n)$ with the constraints that equation 11 is satisfied for every n we may do so by introducing a sequence of Lagrange parameters μ_n and minimizing

$$\Lambda(\mu_1, \mu_2, \dots) = \text{Tr}(D_n [\log D_n - \sum \mu_n a_n^\dagger a_n]) \quad (12)$$

without constraints (except for overall normalization). The operator D_n which yields the minimum is:

$$D_n = \frac{e^{-\sum \mu_n a_n^\dagger a_n}}{\text{Tr}(e^{-\sum \mu_n a_n^\dagger a_n})} \quad (13)$$

Since: $e^{-\sum \mu_n a_n^\dagger a_n} = e^{-\mu_n a_n^\dagger a_n}$ the parameter μ_n is determined by the equation:

$$\bar{N}_n = \frac{\text{Tr}(a_n^\dagger a_n e^{-\mu_n a_n^\dagger a_n})}{\text{Tr}(e^{-\mu_n a_n^\dagger a_n})} \quad (14)$$

The trace is easily evaluated, yielding the following relation between

μ_n and $\bar{N}_n$

$$\mu_n = \log \left(\frac{1 + \bar{N}_n}{N_n} \right) \quad (\text{Bosons}) \quad (15a)$$

$$\mu_n = \log \left(\frac{1 - \bar{N}_n}{N_n} \right) \quad (\text{Fermions}) \quad (15b)$$

Using these values for the Lagrange parameters the maximum entropy consistent with the given single-particle distribution turns out to be:

$$S = -k \sum_n \{ \bar{N}_n \log \bar{N}_n - (1 + \bar{N}_n) \log (1 + \bar{N}_n) \} \quad (\text{Bosons}) \quad (16a)$$

$$S = -k \sum_n \{ \bar{N}_n \log \bar{N}_n + (1 - \bar{N}_n) \log (1 - \bar{N}_n) \} \quad (\text{Fermions}) \quad (16b)$$

These results are identical, as they must be, with those one obtains for the equilibrium distribution of ideal quantum gases.⁴ If we write this approximation to the entropy as $S(D_1)$ then we know that:

$$S \leq S(D_1) \quad (17)$$

and thus:

$$F \geq \min_{\Omega} [\text{Tr}(hD_2) - TS(D_1)] \geq \min_{\Omega} [\text{Tr}(hD_2) - TS(D_1)] \quad (18)$$

where, as before, Ω is any set which contains $\mathcal{D}_2$.

Now let us see if we can find a better approximation to S than the "single-particle entropy" $S(D_1)$. From an information-theory point of view we can see that as we incorporate any of the additional information contained in D_2 our approximation for the entropy will improve, that is it will decrease. $\bar{N}_n$ is the expectation value of the number operator $N_n = a_n^\dagger a_n$. From D_2 we may also obtain the

⁴See e.g. A. Sommerfeld, Thermodynamics and Statistical Mechanics, Academic Press, p. 269.

expectation value of N_n^2 . Of course, for a fermion system $N_n^2 = N_n$ and this gives no new information and therefore no improvement in our approximation to the entropy. However, for a boson system $\bar{N}_n^2$ is independent of $\bar{N}_n$ and we may use this extra information. We thus want to maximize

$$S = k \text{Tr}(D_N \log D_N) \quad (19)$$

with the constraints:

$$\text{Tr}(N_n D_N) = \bar{N}_n \quad (20)$$

$$\text{and } \text{Tr}(N_n^2 D_N) = \bar{N}_n^2 \quad \text{for } n = 1, 2, \dots \quad (21)$$

In terms of the 2-matrix (in the ϕ_n representation):

$$\bar{N}_n^2 = D_2(n, n | n, n) + \bar{N}_n^2 \quad (22)$$

Since the N_n are all mutually commuting operators the D_N which maximizes S is diagonal in the number representation and our problem is essentially a classical one. We must maximize

$$S = k \sum_{N_1, N_2, \dots} P(N_1, N_2, \dots) \log P(N_1, N_2, \dots)$$

with the constraints:

$$\sum P(N_1, N_2, \dots) = 1 \quad ,$$

$$\sum N_n P(N_1, N_2, \dots) = \bar{N}_n \quad ,$$

and:

$$\sum N_n^2 P(N_1, N_2, \dots) = \bar{N}_n^2 \quad .$$

The solution of this problem is straightforward. We introduce Lagrange parameters μ_n and ν_n associated with $\bar{N}_n$ and $\bar{N}_n^2$. The maximizing $P(N_1, N_2, \dots)$ is then:

$$P(N_1, N_2, \dots) = \prod_{n=1}^{\infty} Q^{-1}(\mu_n, \nu_n) \exp(-\mu_n N_n - \nu_n N_n^2)$$

where:

$$Q(\mu, \nu) = \sum_{N=0}^{\infty} \exp(-\mu N - \nu N^2) .$$

μ and ν are determined by the condition that:

$$\bar{N}_n = - \frac{\partial \log Q(\mu_n, \nu_n)}{\partial \mu_n}$$

and:

$$\bar{N}_n^2 = - \frac{\partial \log Q(\mu_n, \nu_n)}{\partial \nu_n}$$

Unfortunately, the sum defining $Q(\mu, \nu)$ cannot be evaluated in closed form; at least not by the author.

Entropy and Fluctuations. The entropy of a boson system is intimately related to the fluctuations in the state occupation numbers. A trivial example of this relationship is the fact that the entropy is zero if the fluctuation in each state is zero. For the non-interacting bose gas the energy does not depend upon $\bar{N}_n^2$ and thus the value of $\bar{N}_n^2$ in the equilibrium state is determined purely by entropy considerations. This fact leads to anomalies in the predicted fluctuations for the system at very low temperatures. As $T \rightarrow 0$ an ideal bose gas would

exhibit macroscopic density fluctuations. Such fluctuations do not occur in liquid helium due to the interparticle forces. (They may be easily observed, however in laser light.)

For a boson system with interactions the interaction energy is dependent upon the values of the $\overline{N}_n^2$ and thus the very large values of the fluctuation are suppressed as being too expensive in energy.

Condensed Boson Systems. Below the condensation temperature certain elements of the 2-matrix become very much larger than the others. In particular the element $D(0,0|0,0)$ is of order N^2 while the elements $D_2(0,k|0,k)$ and $D_2(k,-k|0,0)$ are of order N . Elements of the type $D_2(0,k+p|k,p)$ are of order $N^{\frac{1}{2}}$. Certainly the effect on the entropy of these very large elements will have to be taken into account if one hopes to get acceptable results from a variational calculation. Since $D_2(0,0|0,0)$ is just the average of $N_0^2 - N_0$ we have already seen how to incorporate that information in our approximation to the entropy. Incorporating the constraints which involve $D_2(0,k|0,k)$, $D_2(k,-k|0,0)$, and $D_2(0,k+p|k,p)$ leads to very complex mathematical problems unless one resorts to some crude approximations.