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GENERALIZED INTEGRALS OF DENSITY MATRICES AND GREEN'S FUNCTIONS

V. ANDREOU, A. JANNUSSIS and G. GOUDAROULIS

Dept. of Teoretical Physics, University of Patras, Patras

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Abstract: In this paper we calculate generalized integrals density matrices which are expressed in terms of the canonical Bloch matrices and the Green' s functions.

1. Introduction

It is known that the Bloch[1] density matrices $\Psi(\vec{r}', \vec{r}, b)$ play an important role in the calculations involved in many problems of statistical mechanics.

If the Fermi — Dirac occupation number is taken into consideration then we are led to the generalized canonical density matrices[3].

The Green's function plays an important role in statistical mechanics too and is related to the density matrix through an integral transformation of the Laplace type[2] or through another integral transformation of the Magaril Sawinykh[4] type.

Since in many problems of statistical mechanics we are led not only to integrals involving the density matrix $\Psi(\vec{r}', \vec{r}, b)$ and another function $F(\vec{r}')$ but to integrals involving the Green's function $G(\vec{r}', \vec{r}, E)$ and another function $F(\vec{r}')$ as well, we shall calculate the generalized integrals starting with the case of a canonical density matrix.

2. Integrals of the density matrices

The density matrix corresponding to the Hamilton's H operator is defined by the relation

$$\Psi(\vec{r}', \vec{r}, b) = \sum_j \Psi_j^*(\vec{r}')\, e^{-bH}\, \Psi_j(\vec{r}), \tag{2.1}$$

and satisfies the Bloch equation[5)]

$$\frac{\partial \Psi}{\partial b} + H\Psi = 0 \tag{2.2.}$$

under the initial condition

$$\Psi(\vec{r}', \vec{r}, 0) = \delta(\vec{r}' - \vec{r}). \tag{2.3}$$

In (2.1) $b = \frac{1}{k\,T}$, where k is the Bolzmann' s constant and T is the absolute temperature, $\delta(\vec{r}' - \vec{r})$ is Dirac's δ — function.

Using the density matrix $\Psi(\vec{r}'', \vec{r}, b)$ we can now define and calculate the generalized integrals of the form

$$\int \Psi(\vec{r}', \vec{r}, b)\, F(\vec{r}')\, d\vec{r}', \tag{2.4}$$

where $F(r')$ is any function. We can also calculate integrals of the form

$$\int \Psi(\vec{r}', \vec{r}, b)\, \Psi(\vec{r}, \vec{r}', b')\, d\vec{r}, \tag{2.5}$$

or even

$$\int \cdots \int \Psi(\vec{r}_0, \vec{r}_1, b_1)\, \Psi(\vec{r}_1, \vec{r}_2, b_2) \cdots \Psi(\vec{r}_n, \vec{r}, b_n)\, d\vec{r}_1 \cdots d\vec{r}_n. \tag{2.6}$$

From the definition of the density matrix (2.1) and the relations

$$H\Psi_j = E_j \Psi_j, \quad e^{-bH}\Psi_j = e^{-bE_j}\Psi_j, \quad (\Psi_j, \Psi_k) = \delta_{jk}, \tag{2.7}$$

where Ψ_j and E_j are the eigenfunctions and eigenvalues of the operator H respectively, it follows that for the integral (2.5) the relation

$$\int \Psi(\vec{r}', \vec{r}, b)\, \Psi(\vec{r}, \vec{r}'', b')\, d\vec{r} = \sum_{j,k} \int \Psi_j^*(\vec{r}')\, e^{-bH}\, \Psi_j(\vec{r})\, \Psi_k^*(\vec{r})\, e^{-b'H}\, \Psi_k(\vec{r}'')\, d\vec{r} =$$

$$= \sum_{j,k} \Psi_j^*(\vec{r}')\, e^{-bE_j - b'E_k}\, \Psi_k^*(\vec{r}'')\, \delta_{jk} = \tag{2.8}$$

$$= \sum_j \Psi_j^*(\vec{r}')\, e^{-(b+b')E_j}\, \Psi_j(\vec{r}'') = \Psi(\vec{r}'') = \Psi(\vec{r}', \vec{r}'', b + b')$$

holds. Therefore

$$\int \Psi(\vec{r}', \vec{r}, b)\, \Psi(\vec{r}, \vec{r}'', b')\, d\vec{r} = \Psi(\vec{r}', \vec{r}'', b + b'), \tag{2.9}$$

what can be found also in Feynman[5)] (Statistical Mechanics, p. 79).

With the aid of (2.9) the integral (2.6) can be calculated

$$\int \cdots \int \Psi(\vec{r}_0, \vec{r}_1, b_1)\, \Psi(\vec{r}_1, \vec{r}_2, b_2) \cdots \Psi(\vec{r}_n, \vec{r}, b_n)\, d\vec{r}_1 \cdots d\vec{r}_n = \\ = \Psi(r_0, r, \sum_{j=1}^{n} b_j). \tag{2.10}$$

This integral, in case that $b_1 = b_2 = \cdots = b_n = \varepsilon$, with $\varepsilon \to 0$, $n \to \infty$ and the condition $\varepsilon\, n = U$ is used for the definition of the Path integral[5)].

It will be seen, however, that the calculation of the integral (2.4) differs in the various cases.

The integral (2.4) satisfies the Bloch equation (2.2) in the first place, and, under the initial condition (2.3) the function

$$\Psi(\vec{r}, 0) = F(\vec{r}) \tag{2.11}$$

is obtained and the Bloch equation accepts the symbolic solution

$$\Psi(\vec{r}, b) = e^{-bH}\, F(\vec{r}). \tag{2.12}$$

Therefore, we can write

$$\int \Psi(\vec{r}', \vec{r}, b)\, F(\vec{r}')\, d\vec{r}' = e^{-bH}\, F(\vec{r}). \tag{2.13}$$

Another symbolic proof is this: the definition of the density matrix (2.1) and the integral (2.4) give

$$\sum_j \int \Psi_j^*(\vec{r}')\, e^{-bH}\, \Psi_j(\vec{r})\, F(\vec{r}')\, d\vec{r}' = \sum_j e^{-bH}\, \Psi_j(\vec{r}) \int \Psi_j^*(\vec{r}')\, F(\vec{r}')\, d\vec{r}' = \\ = \sum_j e^{-bH}\, a_j\, \Psi_j(\vec{r}) = \sum_j e^{-bE_j}\, a_j\, \Psi_j(\vec{r}), \tag{2.14}$$

where

$$a_j = \int \Psi_j^*(\vec{r}')\, F(\vec{r}')\, d\vec{r}', \tag{2.15}$$

are the coefficients of the expansion of $F(\vec{r})$ with respect to the orthonormal and complete system of the eigenfunctions $\Psi_j(\vec{r})$.

Furthermore the relation $\sum_j e^{-bH} a_j \Psi_j(\vec{r})$ can be written

$$\sum_j e^{-bH} a_j \Psi_j(\vec{r}) = e^{-bH} F(\vec{r}), \tag{2.16}$$

and we are led to (2.13) again.

In this proof, however, the case that in the Hamilton's operator there are parts which will not commute must always be taken into consideration. This holds even for the simple case that $H = \frac{p^2}{2m} + V(\vec{r})$, $|p^2, V(\vec{r})| \neq 0$, in which the relation $e^{-b\left[\frac{p^2}{2m}+V(\vec{r})\right]} \neq e^{-\frac{bp^2}{2m}} e^{-bV(\vec{r})}$ holds.

An integral of this kind can be found in[6] and refers to the case of free electrons in a uniform magnetic field.

For the case of free electrons the proof can be right straightforward. For the operator

$$H = -\frac{\hbar^2}{2m} \sum_k^N \nabla_k^2 \tag{2.17}$$

the density matrix is given by[5]

$$\Psi(\vec{r}_1', \cdots, \vec{r}_N'; \vec{r}_1, \cdots, \vec{r}_N, b) = \left(\frac{m}{2\pi\hbar^2 b}\right)^{\frac{3N}{2}} \cdot \exp\left\{-\frac{m}{2\hbar^2 b}\sum_k (r_k - \vec{r}_k')^2\right\}, \tag{2.18}$$

and the integral (2.4) takes the form

$$\int_{-\infty}^{\infty} \cdots \int \left(\frac{m}{2\pi\hbar^2 b}\right)^{\frac{3N}{2}} \cdot e^{-\frac{m}{2\hbar^2 b}\sum_k (\vec{r}_k - \vec{r}'_k)^2} F(\vec{r}_1', \cdots, \vec{r}_N')\, d\vec{r}_1' \cdots d\vec{r}_N' =$$

$$= \left(\frac{m}{2\pi\hbar^2 b}\right)^{\frac{3N}{2}} \int_{-\infty}^{\infty} \cdots \int e^{-\frac{m}{2\hbar^2 b}\sum_k \vec{r}_k^{\prime\prime 2}} F(\vec{r}_1 + \vec{r}_1'', \cdots, \vec{r}_N + \vec{r}_N'')\, d\vec{r}_1'' \cdots d\vec{r}_N'' =$$

$$= \left(\frac{m}{2\pi\hbar^2 b}\right)^{\frac{3N}{2}} \left(\int_{-\infty}^{\infty} \cdots \int e^{-\frac{m}{2\hbar^2 b}\sum_k \vec{r}_k^{\prime\prime 2} + \sum_k \vec{r}_k'' \vec{\nabla}_k}\, d\vec{r}_1'' \cdots d\vec{r}_N''\right) F(\vec{r}_1, \cdots, \vec{r}_N) =$$

$$= e^{b\frac{\hbar^2}{2m}\sum_k \nabla_k^2} F(\vec{r}_1 \cdots, \vec{r}_N) = e^{-bH} F(\vec{r}_1, \cdots, \vec{r}_N) \tag{2.19}$$

The integrals of this kind are very difficult to calculate when they involve the generalized canonical matrices of Bloch[3]) defined by the relation

$$D(\vec{r}', \vec{r}, b, \zeta) = \sum \frac{\Psi_j^* (\vec{r}') \Psi_j (\vec{r}')}{1 + e^{b(E_j - \zeta)}}, \tag{2.20}$$

where ζ is the Fermi energy, except for the simple case where

$$\int D(\vec{r}', \vec{r}, b, \zeta) \cdot D(\vec{r}, \vec{r}'', b, \zeta) \, d\vec{r} = D(\vec{r}', \vec{r}'', b, \zeta) - \frac{1}{b} \frac{\partial}{\partial \zeta} D(\vec{r}', \vec{r}'', b, \zeta), \tag{2.21}$$

which can be easily proved.

3. Integrals of the Gren's function

The Green's function of a particle in r — space and with energy E is defined as a solution of the inhomogeneous equation

$$(H - E) \, G(\vec{r}', \vec{r}', E) = - \delta (\vec{r} - \vec{r}'), \tag{3.1}$$

where H is the Hamilton's operator.

When the eigenfunctions and the eigenvalues of the operator H (2.7) are known, the Green's function can be defined as

$$G(\vec{r}', \vec{r}, E) = \lim_{\eta \to 0} \sum \frac{\Psi_j^* (\vec{r}') \Psi_j (\vec{r})}{E - E_j + i \eta}. \tag{3.2}$$

With the Green's function we can calculate integrals of the form

$$\int \cdots \int G(\vec{r}_0, \vec{r}_1, E) \, G(\vec{r}_1, \vec{r}_2, E^{(1)}) \cdots G(\vec{r}_N, \vec{r}, E^{(N)}) \, d\vec{r}_1 \cdots d\vec{r}_N \tag{3.3}$$

and of the form

$$\int G(\vec{r}', \vec{r}, E) \, F(\vec{r}') \, d\vec{r}'. \tag{3.4}$$

The integral (3.3) in connection with definition (3.2) gives

$$\lim_{\eta_0, \eta_1, \ldots, \eta_N \to 0} \int \cdots \int \sum_{j_0, j_1 \cdots j_N} \frac{\Psi_{j_0}^* (\vec{r}_0) \Psi_{j_0} (\vec{r}_1)}{E - E_{j_0} + i \eta_0} \cdot \frac{\Psi_{j_1}^* (\vec{r}_1) \Psi_{j_1} (\vec{r}_2)}{E^{(1)} - E_{j_1} + i \eta_1} \cdots$$

$$\cdots \frac{\Psi_{jN}^* (\vec{r}_N) \Psi_{jN} (\vec{r})}{E^{(N)} - E_{j_N} + i \eta_N} \, d\vec{r}_1 \cdots d\vec{r}_N =$$

$$= \lim_{\eta_0, \eta_1, \cdots, \eta_N \to 0} \sum_{j_0, j_1, \cdots, j_N} \frac{\delta_{j_0 j_1} \delta_{j_1 j_2} \cdots \delta_{j_{N-1} j_N} \Psi_{j_0}^*(\vec{r}_0) \Psi_{j_N}(\vec{r})}{(E - E_{j_0} + i\eta_0)(E^{(1)} - E_{j_1} + i\eta_1) \cdots (E^{(N)} - E_{j_N} + i\eta_N)} =$$

$$= \lim_{\eta_0, \eta_1, \cdots, \eta_N \to 0} \sum_{j} \frac{\Psi_j^*(\vec{r}_0) \Psi_j(\vec{r})}{(E - E_j + i\eta_0)(E^{(1)} - E_j + i\eta_1) \cdots (E^{(N)} - E_j + i\eta_N)} =$$

$$= \sum_{n=0}^{N} A_n G(\vec{r}_0, \vec{r}, E^{(n)}), \text{ for } E^0 \equiv E, \tag{3.6}$$

where the coefficients

$$A_n = - \frac{1}{f'(E^{(n)})} \tag{3.6}$$

and

$$f(x) = (E - x)(E^{(1)} - x) \cdots (E^{(N)} - x). \tag{3.7}$$

For $N = 1$, formula (3.5) yields

$$\int G(\vec{r}_0, \vec{r}_1, E) G(\vec{r}_1, \vec{r}, E^{(1)}) \, d\vec{r}_1 = - \frac{1}{E^{(1)} - E} [G(\vec{r}_0, \vec{r}, E^{(1)}) - G(\vec{r}_0, \vec{r}, E)]. \tag{3.8}$$

The case where $E = E^{(1)}$ is also interesting and can be obtained from (3.8) by letting $E^{(1)} \to E$,

$$\int G(\vec{r}_0, \vec{r}_1, E) G(\vec{r}_1, \vec{r}, E) \, d\vec{r}_1 = - \frac{d}{dE} G(\vec{r}_0, \vec{r}, E). \tag{3.9}$$

From (3.5) we can easily obtain the special case $E = E^{(1)} = E^{(N)}$ which gives

$$\int \cdots \int G(\vec{r}_0, \vec{r}_1, E) G(\vec{r}_1, \vec{r}_2, E) \cdots G(\vec{r}_N, \vec{r}, E) \, d\vec{r}_1 \cdots d\vec{r}_N =$$

$$= \frac{(-1)^N}{N!} \frac{d^N}{dE^N} G(\vec{r}_0, \vec{r}, E). \tag{3.10}$$

The case (3.9) is already known and is mentioned in Landsberg's book[1]).

Because of (3.2) the integral (3.4), which can be calculated in an analogous way, gives

$$\sum_j \frac{\Psi_j(\vec{r})}{E - E_j} \int \Psi_j^*(\vec{r}') F(\vec{r}') \, d\vec{r}' = \sum_j \frac{a_j \Psi_j(\vec{r})}{E - E_j}, \tag{3.11}$$

where a_j are the coefficients of the expansion (2.15). Since the right-hand side of (3.11) is obtained by applying the operator $(E-H)^{-1}$ to the function $\sum_j a_j \Psi_j(\vec{r}) = F(\vec{r})$, namely

$$\sum_j \left(\frac{1}{E-H}\right) a_j \Psi_j(\vec{r}) = \sum_j \frac{a_j \Psi_j(\vec{r})}{E-E_j}, \tag{3.12}$$

the integral (3.4) takes the form

$$\int G(\vec{r}', \vec{r}, E)\, F(\vec{r}')\, d\vec{r}' = \left(\frac{1}{E-H}\right) F(\vec{r}). \tag{3.13}$$

The case where the function $F(\vec{r}')$ is the density matrix (2.1) itself, gives

$$\int G(\vec{r}_0, \vec{r}, E)\, \Psi(\vec{r}, \vec{r}', b)\, d\vec{r} = \sum_j \frac{\Psi_j^*(\vec{r}_0)\, e^{-bE_j}\, \Psi_j(\vec{r}')}{E-E_j}. \tag{3.14}$$

The distribution

$$\Gamma(\vec{r}', \vec{r}, b, E) = \sum_j \frac{\Psi_j^*(\vec{r}')\, e^{-bE_j}\, \Psi_j(\vec{r})}{E-E_j} \tag{3.15}$$

appears for the first time and is believed to have certain applications. For $b=0$, i. e. for high temperature, it coincides with Green function, whereas for $E=0$ it leads to the integral of the density matrix with respect to the parameter b.

The distribution (3.15) can be written as

$$\Gamma(\vec{r}', \vec{r}, b, E) = \lim_{\eta \to 0} \sum_j \frac{\Psi_j^*(\vec{r}')\, e^{-b(E+i\eta)}\, [(e^{b(E-E_j+i\eta)} - 1) + 1]\, \Psi_j(\vec{r})}{E - E_j + i\eta} =$$

$$= \lim_{\eta \to 0} e^{-b(+i\eta)}\, G(\vec{r}', \vec{r}, E) + e^{-bE} \int_0^b e^{b'E}\, \Psi(\vec{r}', \vec{r}, b',)\, db'. \tag{3.16}$$

Another expression of the above distribution is derived by means of the integral

$$\int_0^\infty e^{\frac{it}{\hbar}(E-E_j+i\eta)}\, dt, \tag{3.17}$$

that is

$$\Gamma(\vec{r}', \vec{r}, b, E) = \lim_{\eta \to 0} \frac{1}{\hbar i} \sum_j \Psi_j^* (\vec{r}') \int_0^\infty e^{\frac{it}{\hbar}(E - E_j + i\eta)} dt\, e^{-bE_j} \Psi_j (\vec{r}) =$$

$$= \lim_{\eta \to 0} \frac{1}{i\hbar} \int_0^\infty e^{\frac{it}{\hbar}(E + i\eta)} \Psi\left(\vec{r}', \vec{r}, b + \frac{it}{\hbar}\right) dt = \tag{3.18}$$

$$= \lim_{\eta \to 0} \frac{1}{E + i\eta + \frac{\partial}{\partial b}} \cdot \Psi(\vec{r}', \vec{r}, b).$$

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