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AN APPROXIMATE SOLUTION OF THE BLOCH EQUATION

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Abstract: In this paper it is proved that if for the operator $\mathscr{H}_0$ the density matrix is known, the solution of the Bloch equation for the operator $\mathscr{H} = \mathscr{H}_0 + \mathscr{H}_1$ is given in terms of a powers series in $b = \frac{1}{KT}$.

1. Introduction

It is known[1)] that all the thermodynamic properties of a system are given by the partition function

$$z(b) = Tr\, e^{-b\mathscr{H}} \tag{1}$$

where $\mathscr{H}$ is the Hamilton operator and $b = \frac{1}{KT}$, K is the Boltzmann constant and T is the absolute temperature.

When the density matrix

$$\psi(\vec{r}', \vec{r}, b) = \sum_j \psi_j^* (\vec{r}')\, e^{-b\mathscr{H}}\, \psi_j (\vec{r}) \tag{2}$$

is known, the partition function $z(b)$ is given by the formula

$$z(b) = \sum_j e^{-bE_j} = \int \psi(\vec{r}, \vec{r}, b)\, d\vec{r}. \tag{3}$$

The density matrix (2) satisfies the Bloch equation[2], that is

$$\frac{\partial \psi}{\partial b} + \mathscr{H} \psi = 0, \tag{4}$$

with the initial condition

$$\psi (\vec{r}', \vec{r}, 0) = \sigma (\vec{r}' - \vec{r}). \tag{5}$$

The solution of the Bloch equation has attracted the interest of many authors and the result was the development of various methods of which most important can be found in a book by Münster[1]. These are:

— Cluster expansion method, which was developed by Montroll-Ward[3] with the use of the Green function;

— high temperature method, which consists of expanding in power series of Planck's constant h, of which the first term corresponds to the semi classical expression. This method was developed by Wigner[4], Kirkwood[5] and by Goldberger and Adams[6]; and

— low temperature expansion method which has been developed by Goldberger and Adams[6].

Recently Morita[7] gave the solution of the Bloch equation for a many particle system in a box, in terms of the path integral.

The method of the path integral has been applied in statistical mechanics by Siegel and Burke[8]. We cannot obtain an exact solution of the Bloch equation (4) except for certain form of the potential energy. The case of the harmonic oscillator has been studied by Davies[9] and the case of free-electron in a uniform magnetic field by Sondheimer-Wilson[10]. Jannussis[11] gave an exact solution of the Bloch equation for the case of a free-electron in uniform electric and magnetic fields.

Here another method is developed which has been used by Jannussis[12] for the one dimensional case and which consists of a dirct expansion in power series of $b = \frac{1}{KT}$ and is valid for high temperatures.

2. *Solution of the Bloch equation in three dimensions*

The Bloch equation in thrce dimensions has thc form

$$\frac{\partial \psi}{\partial b} = \frac{\hbar^2}{2m} \Delta \psi - V(\vec{r}) \psi = \left\{ \frac{\hbar^2}{2m} \Delta - V(\vec{r}) \right\} \psi, \tag{6}$$

where $V(\vec{r})$ is the potential energy. The required solution $\psi(\vec{r}, b)$ of (6) for $b = 0$ must satisfy the initial condition

$$\psi(\vec{r}, 0) = F(\vec{r}), \tag{7}$$

where $F(\vec{r})$ is an arbitrary function. If we suppose that the solution of (6) can be expanded in a series of the form

$$\psi(\vec{r}, b) = \sum_{n=0}^{\infty} \psi_n(\vec{r})\, b^n, \tag{8}$$

the functions $\psi_n(\vec{r})$ should satisfy the following differential system

$$(n' + 1)\, \psi_{n+1}(\vec{r}) = \mathscr{H}\, \psi_n(\vec{r}) = \left(\frac{\hbar^2}{2m} \Delta - V(\vec{r})\right) \psi_n(\vec{r}), \tag{9}$$

where $\mathscr{H} = -\frac{\hbar^2}{2m} \Delta + V(\vec{r})$ is the Hamilton operator.

The solution of the system (9) can be obtained for $n = 0, 2, 1, \ldots$ provided that $\psi_0(\vec{r}) \neq 0$.

The function $\psi_1(\vec{r})$ is given by the expression

$$\psi_1 = -\mathscr{H}\, \psi_0 = \frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2}\psi_0 = \frac{\partial^2}{\partial y^2}\psi_0 + \frac{\partial^2}{\partial z^2}\psi_0\right) - V(\vec{r})\, \psi_0(\vec{r}). \tag{10}$$

Likewise, for $n = 1$ we get

$$\psi_2(\vec{r}) = \frac{1}{2!}\left\{\left(\frac{\hbar^2}{2m}\Delta\right)^2 - \frac{\hbar^2}{2m}\left(V(\vec{r})\,\Delta + \Delta\, V(\vec{r})\right) + V^2(\vec{r})\right\} \psi_0(\vec{r}). \tag{11}$$

Consequently the solution (8) of the Bloch equation has the form

$$\psi(\vec{r}, b) = \psi_0(\vec{r}) + \frac{b}{1!}\left\{\frac{\hbar^2}{2m}\Delta - V(\vec{r})\right\} \psi_0(\vec{r}) + \frac{b^2}{2!}\left\{\left(\frac{\hbar^2}{2m}\Delta\right)^2 - \right.$$

$$\left. - \frac{\hbar^2}{2m}\left(V(\vec{r})\,\Delta + \Delta\, V(\vec{r})\right) + V^2(\vec{r})\right\} \psi_0(\vec{r}) + \ldots . \tag{12}$$

In the above solution, there appear the series

$$\left(\sum_{n=0} \frac{b^n}{n!}\left(\frac{\hbar^2}{2m}\Delta\right)^n \psi_0(\vec{r}), \quad \sum_n \frac{(-V(\vec{r}))^n}{n!}\psi_0(\vec{r}) \tag{13}$$

together with other terms containing the function $\psi_0(\vec{r})\, V(\vec{r})$ and their derivatives. Furthermore, it can be proved that

$$\sum \frac{b^n\left(\frac{\hbar^2}{2m}\Delta\right)^n}{n!}\psi_0(\vec{r}) = \frac{1}{\left(4\pi b\frac{\hbar^2}{2m}\right)^{\frac{3}{2}}}\int \psi_0(\vec{r}')\, e^{-\frac{(\vec{r}-\vec{r}')^2}{4b\frac{\hbar^2}{2m}}}\, d\vec{r}' =$$

$$= e^{b\frac{\hbar^2}{2m}\Delta}\psi_0(\vec{r}), \tag{14}$$

which, for the case of one dimension, has been given by Born and Ludwig[13]. Moreover any function $\psi_0(\vec{r})$ must be subject to the kown restrictions.

Hence the required solution of the Bloch equation in the form of a power series of b, will be

$$\psi(\vec{r}, b) = \int \psi_0(\vec{r}')\, \psi(r, \vec{r}', b)\, dr' + (e^{-bV(\vec{r})} - 1)\,\psi_0(\vec{r}) + 0(b^2), \tag{15}$$

where $\psi(\vec{r}, \vec{r}', b)$ is the density matrix of the operator $-\frac{\hbar^2}{2m}\Delta$, namely the Green function of the free electron[14]

$$\psi(\vec{r}, \vec{r}', b) = \left(\frac{m}{2\pi b\hbar^2}\right)^{\frac{3}{2}} e^{-\frac{m(\vec{r}-\vec{r}')^2}{2b\hbar^2}}. \tag{16}$$

The above results (15) can be extended to the case of $3N$ dimensions, that is

$$\psi(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N, b) =$$

$$= \left(\frac{m}{2\pi b\hbar^2}\right)^{\frac{3N}{2}} \int \psi_0(\vec{r}_1', \vec{r}_2', \ldots, \vec{r}_N')\, e^{-\frac{m}{2b\hbar^2}\sum_{j=1}^{N}(\vec{r}_j-\vec{r}_j')^2}\, d\vec{r}_1 \ldots d\vec{r}_N' +$$

$$+ (e^{-bV(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N)} - 1)\,\psi_0(\vec{r}_1, \ldots, \vec{r}_N) + 0(b^2). \tag{17}$$

It can be easily proved that for $b = 0$ the initial condition (5) holds. Also for $V(\vec{r}) = 0$ the solution for the free-particles is readily obtained.

3. Solution of the Bloch equation in three dimensions and in a uniform magnetic and electric fields

The Bloch equation in three dimensions, and in a uniform magnetic field H, is

$$\frac{\partial \psi}{\partial b} + \{\mathscr{H}_0 + V(\vec{r})\}\,\psi = 0, \tag{18}$$

where

$$\mathscr{H}_0 = \frac{1}{2m}(\vec{p} - \frac{e}{c}\vec{A}(\vec{r}))^2 - e(\vec{E}, \vec{r}); \tag{19}$$

$A(\vec{r})$ is the vector potential and $\vec{E}$ is the electric field.

For a symmetric vector potential of the form $A(\vec{r}) = \left(-\frac{1}{2}Hy, \frac{1}{2}Hx, 0\right)$ the equation (18) reduces to

$$\frac{\partial \psi}{\partial b} + \left\{-\frac{\hbar^2}{2m}\Delta - i\mu H\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right) - \frac{e^2 H^2}{8mc^2}(x^2 + y^2) + V(\vec{r}) + e(\vec{E}, \vec{r})\right\}$$

$$\psi = 0, \tag{20}$$

where $\mu = \frac{e\hbar}{2m}$ is the Bohr magneton.

Using the argument of the foregoing paragraph, we obtain

$$\psi(\vec{r}, b) = \int \psi(\vec{r}', \vec{r}, b)\,\psi_0(\vec{r}')\,d\vec{r}' + (e^{-bV(\vec{r})} - 1)\,\psi_0(r) + 0(b^2), \tag{21}$$

where $\psi(\vec{r}', \vec{r}, b)$ is the density matrix of the operator $\mathscr{H}_0$, which was given by Jannussis[11] and has the form

$$\psi(\vec{r}', \vec{r}, b) = \left(\frac{m}{2\pi\hbar^2 b}\right)^{\frac{3}{2}} \frac{\mu H b}{\sinh \mu H b}\, e^{f(b) - e(\vec{E}\vec{r}')b} \exp - \frac{m}{2b\hbar^2}\{2i\mu h b(x'y -$$

$$- xy') + (z - z')^2 + \mu H b \coth \mu H b((x - x')^2 + (y - y')^2) -$$

$$- e\frac{E_z b}{2}(z - z') - e\left\{\frac{E_x}{2}b - i\frac{E_y}{2\mu H}(1 - \mu H b \coth \mu H b)\right\}(x - x') -$$

$$e\left\{\frac{E_y}{2}b + i\frac{E_x}{2\mu H}(1 - \mu H b \coth \mu H b)\right\}(y - y'). \quad (22$$

For $\vec{E} = 0$ (22) reduces to the density matrix of Sondheimer-Wilson[10].

The integral $\int \psi(\vec{r}', \vec{r}, b)\, \psi(r')\, dr'$, in which $\psi(\vec{r}'\, \vec{r}, b)$ is the density matrix of free electrons in a uniform magnetic field, can be calculated

$$\int \psi(\vec{r}', \vec{r}, b)\, \psi_0(\vec{r}')\, d\vec{r}' = \frac{1}{\cosh \mu H b}\, e^{-\frac{b\left\{\frac{e^2 H^2}{8 m c^2}(x^2 + y^2)\right\}}{\mu H b \coth \mu H b}}$$

$$e^{\frac{b}{\mu H b \coth \mu H b}\left\{\frac{\hbar^2}{2m}\Delta + i \mu H \left(x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x}\right)\right\}}\, \psi_0(r). \tag{23}$$

The expression (21) for $V(\vec{r}) = 0$ leads to the known solution of the Bloch equation, of the form

$$\psi(\vec{r}, b) = \int \psi(\vec{r}', \vec{r}, b)\, \psi_0(\vec{r}')\, d\vec{r}' \tag{24}$$

also, the (21) for the case of $\vec{H} \to 0$ and $\vec{E} \to 0$ leads to (17). The same holds for the integral (23).

From the above argument, we conclude that: if for the operator $\mathscr{H}_0$ the density matrix is known, the solution of the Bloch equation for the operator $\mathscr{H} = \mathscr{H}_0 + \mathscr{H}_1$ is given by the form

$$\psi(\vec{r}, b) = \int \psi(\vec{r}', \vec{r}, b)\, \psi_0(\vec{r}')\, d\vec{r}' + \left(e^{-b \mathscr{H}_1(\vec{r})} - 1\right) \psi_0(\vec{r}) + 0(b^2). \tag{25}$$

The above solution can be extended in the case of n particles and the solution is of the form

$$\psi(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_n, b) = \int \psi(\vec{r}_1', \vec{r}_2', \ldots, \vec{r}_n';$$

$$\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_n, b)\, \psi_0(\vec{r}_1', \vec{r}_2', \ldots, \vec{r}_n')\, d\vec{r}_1'\, d\vec{r}_2' \ldots d\vec{r}_n' + \left(e^{-b \mathscr{H}_1(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_n)} - \right.$$

$$\left. - 1\right) \psi_0(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_n) + 0(b^2). \tag{26}$$

This solution is simple and can be applied to many problems, provided that the density matrix of the operator $\mathscr{H}_0$ is known. An important example is the case of the spherical harmonic oscillator, because then the density matrix is known[14] and has the form

$$\psi(\vec{r}', \vec{r}, b) = \left\{\frac{m\omega}{2\pi h \sinh \hbar \omega b}\right\}^{\frac{3}{2}} e^{\frac{m\omega}{2\hbar \sinh \hbar \omega b}\left[(\vec{r}^2 + \vec{r}'^2) \cosh \hbar \omega b - 2\vec{r}\, \vec{r}'\right]} \tag{27}$$

For $\omega \to 0$ (27) reduces to the density matrix of the free particle.

Using the density matrix (27) we can easily calculate the density matrix of a spherical harmonic oscillator in a uniform electric field. The density matrix has the following form

$$\psi_{\vec{E}\neq 0}(\vec{r}'\,\vec{r}, b) = \left(\frac{m\,\omega}{2\pi\, h \sinh \hbar\,\omega\, b}\right)^{\frac{3}{2}} e^{-\frac{m\omega}{2h \sinh \hbar\,\omega b}|(\vec{r}^2+\vec{r}'^2)\cosh \hbar\omega b - 2\vec{r}\,\vec{r}'|} -$$

$$- e^{-\frac{eE}{\hbar\omega}\operatorname{tgh}\frac{\hbar\omega b}{2}(\vec{r}+\vec{r}') + \frac{e^2E^2}{m\hbar\omega^3}\left\{\frac{\hbar\omega b}{2} - \operatorname{tgh}\frac{\hbar\omega b}{2}\right\}}. \tag{28}$$

The above solution, when $b \to 0$, satisfies the initial condition $\psi_{\vec{E}\neq 0}(\vec{r}', \vec{r}, 0) = \delta(\vec{r} - \vec{r}')$ and by $\omega \to 0$ reduces to

$$\psi_{\vec{E}\neq 0}(\vec{r}', \vec{r}, b) = \left(\frac{m}{2\pi\,\hbar^2\, b}\right)^{\frac{3}{2}} - e^{\frac{\hbar^2 e^2}{24\, m}E^2 b^3 - \frac{m}{2\hbar^2 b}(\vec{r} - \vec{r}')^2 - \frac{e\,b}{2}E(\vec{r} + \vec{r}')}, \tag{29}$$

which is exactly the density matrix of an electron in a uniform electric field[11].

When $\vec{r} = \vec{r}'$, (29) gives

$$\psi_{\vec{E}\neq 0}(\vec{r}, \vec{r}, b) = \left\{\frac{m\,\omega}{2\pi\, h \sinh \hbar\,\omega\, b}\right\}^{\frac{3}{2}} e^{-\frac{m\omega}{\hbar}\operatorname{tgh}\frac{\hbar\omega b}{2} r^2 - \frac{2e\vec{E}}{\hbar}\operatorname{tgh}\frac{\hbar\omega b}{2}\vec{r}}$$

$$e^{\frac{e^2E^2}{m\hbar\omega^3}\left\{\frac{\hbar\omega b}{2} - \operatorname{tgh}\frac{\hbar\omega b}{2}\right\}}$$

and the partition function is derived from (30)

$$Z(b) = \frac{1}{\left\{2 \sinh \frac{\hbar\,\omega\, b}{2}\right\}^3} e^{\frac{e^2E^2 b}{2m\omega^2}}. \tag{31}$$

The free energy has the form

$$F = \frac{3}{2}\hbar\,\omega + 3\,K\,T \ln\left(1 - e^{-\frac{\hbar\omega}{KT}}\right) - \frac{e^2\,E^2}{2m\omega^2}. \tag{32}$$

Now we examine the limit of high temperature or small b in Equ. (30). In this limit

$$\psi_{\vec{E}\neq 0}(\vec{r}, \vec{r}', b) \to e^{-\frac{m\,\omega^2}{2KT}r^2 - \frac{e\vec{E}}{KT}\vec{r}}\, e^{-\frac{V(\vec{r})}{KT}}, \tag{33}$$

where

$$V(r) = \frac{m}{2}\omega^2 r^2 + \mathscr{E}(E\,r) \tag{34}$$

except for the factor in front of the exponential. This result (34), agrees with classical mechanics.

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PRIBLIŽNO RJEŠENJE BLOCH-ove JEDNADŽBE

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Sadržaj

U radu je pokazano, da se uz poznatu matricu gustoće za operator $\mathscr{H}_0$, rješenje Blochove jednadžbe za operator $\mathscr{H} = \mathscr{H}_0 + \mathscr{H}_1$ može prikazati redom potencija od $b = \frac{1}{KT}$.