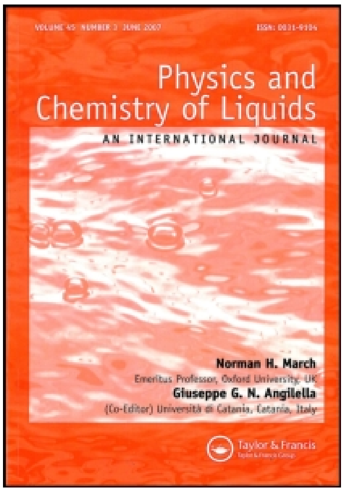

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SLATER SUM AND KINETIC ENERGY TENSOR IN SOME SIMPLE INHOMOGENEOUS ELECTRON LIQUIDS

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Starting from the Bloch equation for the canonical density matrix, the differential equation satisfied by the Slater sum is derived for some simple inhomogeneous electron liquids. The relation of this derivation to the differential form of the virial theorem, and in particular to the kinetic energy tensor, is finally discussed.

KEY WORDS: Bloch equation, slater sum, kinetic energy tensor.

1. INTRODUCTION

Since the work of March and Murray[1], specifically for central field problems, it has been known that the Bloch equation for the canonical density matrix contains within itself a differential equation for the Slater sum $P(\mathbf{r}, \beta)$. Here, for independent electrons moving in a common potential energy $V(\mathbf{r})$, $P(\mathbf{r}, \beta)$ is defined in terms of the one-electron eigenvalues ε_i and the corresponding one-electron wave functions $\psi_i(\mathbf{r})$ by

$$P(\mathbf{r}, \beta) = \sum_{\text{all}\, i} \psi_i(\mathbf{r}) \psi_i^*(\mathbf{r}) e^{-\beta\epsilon_i} \quad : \quad \beta = 1/k_B T \tag{1.1}$$

where $k_B T$ is the thermal energy. The canonical density matrix $C(\mathbf{r}_1, \mathbf{r}_2, \beta)$ is the direct generalization of eqn (1.1) to the off-diagonal form

$$C(\mathbf{r}_1, \mathbf{r}_2, \beta) = \sum_{\text{all}\, i} \psi_i(\mathbf{r}_1) \psi_i^*(\mathbf{r}_2) e^{-\beta\epsilon_i} \tag{1.2}$$

If $\hat{H}$ denotes the independent Hamiltonian of the inhomogeneous electron liquid defined by the application of the one-body potential energy $V(\mathbf{r})$:

$$\hat{H}(\mathbf{r}) = -\frac{1}{2}\nabla_{\mathbf{r}}^2 + V(\mathbf{r}) \tag{1.3}$$

then one will take us starting point the appropriate Bloch equations (see eqns (2.1) and (2.2) below). The differential equation for $P(\mathbf{r}, \beta)$ for some simple cases will then be derived by direct expansion of the canonical density matrix about its diagonal. After this development, the connection with the differential form of the virial theorem[2], and in particular with the kinetic energy tensor, will be considered in section 3. Section 4 constitutes a brief summary, with some proposals for future work.

2. DIFFERENTIAL EQUATION FOR SLATER SUM $P(\mathbf{r}, \beta)$ IN SOME SIMPLE CASES

The starting point of the present derivation will be the two forms of the Bloch equation for C defined in eqn (1.2):

$$\left[-\frac{1}{2}\nabla_1^2 + V(\mathbf{r}_1)\right] C(\mathbf{r}_1, \mathbf{r}_2, \beta) = -\frac{\partial}{\partial \beta} C(\mathbf{r}_1, \mathbf{r}_2, \beta) \tag{2.1}$$

$$\left[-\frac{1}{2}\nabla_2^2 + V(\mathbf{r}_2)\right] C(\mathbf{r}_1, \mathbf{r}_2, \beta) = -\frac{\partial}{\partial \beta} C(\mathbf{r}_1, \mathbf{r}_2, \beta) \tag{2.2}$$

Introducing new independent variables as $\mathbf{R} = \frac{1}{2}(\mathbf{r}_1 + \mathbf{r}_2)$ and $\mathbf{r}_{12} = \mathbf{r}_1 - \mathbf{r}_2$, summing and subtracting eqns (2.1) and (2.2), one finds

$$\left[-\frac{1}{4}\nabla_R^2 - \nabla_{12}^2 + 2V(\mathbf{R})\right] C(\mathbf{r}_1, \mathbf{r}_2, \beta) = -2\frac{\partial}{\partial \beta} C(\mathbf{r}_1, \mathbf{r}_2, \beta) \tag{2.3}$$

$$\vec{\nabla}_R \cdot \vec{\nabla}_{12} C(\mathbf{r}_1, \mathbf{r}_2, \beta) = \mathbf{r}_{12} \cdot \vec{\nabla} V(\mathbf{R}) C(\mathbf{r}_1, \mathbf{r}_2, \beta) \tag{2.4}$$

in the limit $\mathbf{r}_{12} \to 0$. Now

$$\nabla_R^2 = \frac{1}{R^2}\frac{\partial}{\partial R} R^2 \frac{\partial}{\partial R}$$

and

$$\vec{\nabla}_{12} = \frac{\mathbf{r}_{12}}{r_{12}}\frac{\partial}{\partial r_{12}} + \frac{1}{r_{12}}\left(\frac{\mathbf{R}}{R} - \mu\frac{\mathbf{r}_{12}}{r_{12}}\right)\frac{\partial}{\partial \mu}$$

$$\nabla_{12}^2 = \frac{1}{r_{12}^2}\frac{\partial}{\partial r_{12}} r_{12}^2 \frac{\partial}{\partial r_{12}} + \frac{1}{r_{12}^2}\frac{\partial}{\partial \mu}(1-\mu^2)\frac{\partial}{\partial \mu}$$

with

$$\mu = \frac{\mathbf{R} \cdot \mathbf{r}_{12}}{R r_{12}}$$

Taking as the first example the case of a bare Coulomb field, i.e. $V(R) = -Z/r$, Blinder's arguments[3] lead to

$$C(\mathbf{r}_1, \mathbf{r}_2, \beta) = P\left[\frac{1}{2}(r_1 + r_2), \beta\right] + \Delta\left[\frac{1}{2}(r_1 + r_2), \beta\right] r_{12}^2 + o(r_{12}^4)$$

$$= P(R, \beta) + \left[\frac{(1-\mu^2)}{8R}\frac{\partial P}{\partial R} + \Delta(R, \beta)\right] r_{12}^2 + o(r_{12}^4) \tag{2.5}$$

while eqns (2.3) and (2.4) become, respectively,

$$\frac{1}{8}P'' + \frac{1}{2R}P' - \left(V + \frac{\partial}{\partial\beta}\right)P + 3\Delta = 0 \tag{2.6}$$

and

$$\Delta' = \frac{1}{2}V'P + \frac{1}{4R^2}P'. \tag{2.7}$$

One then finds, differentiating eqn (2.6) and inserting Δ' from eqn (2.7), for the Slater sum $P(R, \beta)$

$$\frac{1}{8}P''' + \frac{1}{2R}P'' + \left(\frac{1}{4R^2} - V - \frac{\partial}{\partial\beta}\right)P' + \frac{1}{2}V'P = 0. \tag{2.8}$$

This equation is solved by $P(R, \beta \to \infty) = e^{-2ZR + \beta Z^2/2}$.

Using similar arguments and puting (see Sondheimer and Wilson[4])

$$C(\mathbf{r}_1, \mathbf{r}_2, \beta) = P(R, \beta) + \Delta(R, \beta) r_{12}^2 + o(r_{12}^4) \tag{2.9}$$

for the harmonic potential in three dimensions, the differential equation for the Slater sum is

$$\frac{1}{8}P''' + \frac{1}{4R}P'' - \left(\frac{1}{4R^2} + V + \frac{\partial}{\partial\beta}\right)P' + \frac{1}{2}V'P = 0. \tag{2.10}$$

Finally we have considered also the case of a uniform electric field of arbitrary strength along x-axis in three dimensions. In this case the near-diagonal form for C (see Harris and Cina[5], Jannussis[6])

$$C(\mathbf{r}_1, \mathbf{r}_2, \beta) = P(X, \beta) + \Delta(X, \beta) r_{12}^2 + o(r_{12}^4) \tag{2.11}$$

leads to the following differential equation

$$\frac{1}{8}P''' - \left(V + \frac{\partial}{\partial\beta}\right)P' + \frac{1}{2}V'P = 0. \tag{2.12}$$

It is evident, comparing these last two results with the corresponding one dimensional equations, that the dimensionality D gives the coefficient $(D-2)/2$ to the term $V'P$. In a general central field the independent variables are r_1, r_2 and r_{12} giving a greater freedom to the form (2.5) that now can be written

$$C(\mathbf{r}_1, \mathbf{r}_2, \beta) = P(R, \beta) + [\Delta_1(R, \beta) + \mu^2 \Delta_2(R, \beta)] r_{12}^2 + o(r_{12}^4) \tag{2.13}$$

and eqns (2.3) and (2.4) are probably not sufficient to give separate equations for P, Δ_1 and Δ_2. The additional condition

$$C(\mathbf{r}_1, \mathbf{r}_2, \beta + \beta') = \int C(\mathbf{r}_1, \mathbf{r}, \beta)\, C(\mathbf{r}, \mathbf{r}_2, \beta')\, d\mathbf{r}$$

for β' small leads back to the Bloch equation and does not give further information.

3. DIFFERENTIAL FORM OF THE VIRIAL THEOREM

We did some analyses of our previous results and we arrived at the conclusion that the differential form of the virial theorem is already included in eqns. (2.3) and (2.4). The function Δ should be also related directly to the trace of the kinetic energy tensor. The form (2.5) in this context can be read as

$$C(\mathbf{r}_1,\mathbf{r}_2,\beta)=P(R,\beta)+\frac{1}{2}\mathbf{r}_{12}\cdot\mathbf{T}(R,\beta)\cdot\mathbf{r}_{12}+\ldots \tag{3.1}$$

where

$$T_{ij}=\lim_{r_{12}\to 0}\frac{1}{2}\left(\frac{\partial^2 C}{\partial x_{i1}\partial x_{j2}}+\frac{\partial^2 C}{\partial x_{j1}\partial x_{i2}}\right) \tag{3.2}$$

is, by definition, a kinetic energy tensor. This tensor must satisfy the differential form of the virial theorem that, for a general central field, could be expressed as a relation of the following type[2]

$$R_i f[V,P]=\sum_{j=1}^{3}\frac{\partial T_{ij}}{\partial R_j}\quad (i=1,2,3). \tag{3.3}$$

Again, from Blinder's arguments, in the Coulomb field the kinetic energy tensor can be written in terms of the trace t, being

$$T_{ij}=t\frac{R_i R_j}{R^2} \tag{3.4}$$

and eqn (3.3) reduces to the following scalar relation

$$f[V,P]=\frac{1}{R}t+t' \tag{3.5}$$

which can be combined with the definition of the kinetic energy density to give an equation for the Slater sum. In a general central field the matrix elements of $\mathbf{T}$ are not related simply to the trace. After some derivation the result was the following. Writing[1]

$$C(\mathbf{r}_1,\mathbf{r}_2,\beta)=\sum_{nl}\chi_{nl}(r_1)\chi_{nl}(r_2)a_{nl}(\cos\theta,\beta) \tag{3.6}$$

one has

$$T_{ij}=\frac{1}{2}\left[\delta_{ij}-\frac{R_i R_j}{R^2}\right]t(R,\beta)+\frac{1}{4}\left[\frac{3R_i R_j}{R^2}-\delta_{ij}\right]s(R,\beta) \tag{3.7}$$

where

$$s(R,\beta)=\sum_{nl}\chi'_{nl}(R)\chi'_{nl}(R)a_{nl}(1,\beta) \tag{3.8}$$

Now eqn (3.7) should be the most general form in central field; one has a new function $s(R,\beta)$ and precisely the same condition as in eqn (2.13).

4. SUMMARY AND FUTURE DIRECTIONS

It has been shown, by a direct argument from the Bloch equations (2.1) and (2.2) for the canonical density matrix, that the differential equations (2.8) and (2.10) for the Coulomb field and the harmonic oscillator respectively can be simply obtained. The differential equation (2.8) for the Coulomb field has also been recently obtained by Pfalzner *et al.*[7] and Cooper[8] by means of the spatial generalization of Kato's theorem[9]. Again, a different derivation has been given from that of Lehmann and March[10] for initially free electrons in a uniform electric field of arbitrary strength. The connection of the arguments of section 2 with the differential form of the virial theorem is set out in section 3. For the specific case of the Coulomb field, this is directly connected with a relation, eqn. (3.4), between the kinetic energy tensor (3.2) and the trace t, of central importance in density functional theory.

We are currently working on the generalization of these arguments to treat the case of a hydrogen-like atom in an electric field of arbitrary strength. Directions in which this is being tackled are (i) semiclassical approaches (see Hill[11] and Blinder[12]) and (ii) fully quantal approaches using the separability in parabolic coordinates. Undoubtedly, in the Coulomb problem in zero electric field, the separability, of the Schrödinger wave equation in both spherical polar coordinates and also parabolic coordinates can be subsumed into the existence of the Runge-Lenz vector as a constant of motion additional to the conventional ones in central fields. Generalizations are being sought presently for non-zero electric field.

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