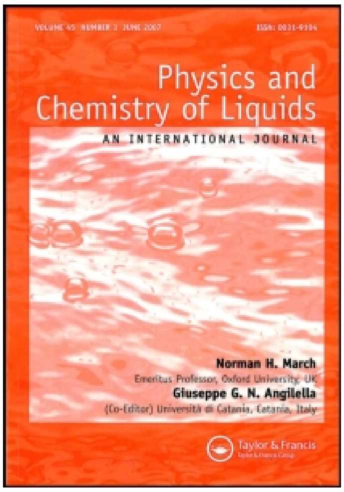

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LETTER

Differential Equation for Slater Sum in an Inhomogeneous Electron Liquid

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For independent electrons moving in a one-body potential $V(\mathbf{r})$ of arbitrarily low symmetry, a partial differential equation is set up for the Slater sum $Z(\mathbf{r}, \beta)$, where $\beta = (k_B T)^{-1}$. As an example, the case when $V(\mathbf{r})$ is the result of an applied time-independent and spatially constant electric field of arbitrary strength is briefly considered.

KEY WORDS: Bloch equation, Thomas-Fermi theory.

The fact that the canonical density matrix satisfies the Bloch equation has been known for a long time. However, it was subsequently shown by March and Murray[1], specifically for central field problems, that the diagonal element of the canonical density matrix, the so-called Slater sum $Z(\mathbf{r}, \beta)$, itself satisfied a differential equation, though of higher order than the Bloch equation.

In the course of work on atoms and molecules in intense external fields, we have found that such a differential equation can be set up for independent electrons moving in a one-body potential energy $V(\mathbf{r})$ of arbitrarily low symmetry. The purpose of this Letter is to present the derivation of this equation, and to exemplify its use by considering, quite briefly, the case when $V(\mathbf{r})$ arises solely from an applied electric field, constant in space and time, of arbitrary intensity.

Let us begin by summarizing the definition of the Slater sum $Z(\mathbf{r}, \beta)$. Suppose that the eigenfunctions $\psi_i(\mathbf{r})$ and corresponding eigenvalus ε_i are generated by the one-body potential $V(\mathbf{r})$. Then the Slater sum is defined by

$$Z(\mathbf{r},\beta) = \sum \psi_i(\mathbf{r})\psi_i^*(\mathbf{r}) \exp(-\beta\varepsilon_i) \tag{1}$$

where $\beta = (k_B T)^{-1}$.

As a first step, let us form the Thomas-Fermi approximation to Z. This may be written from Eq. (1) as

$$Z_{TF}(\mathbf{r},\beta) \simeq Z_0^{(D)}(\beta)\exp(-\beta V(\mathbf{r})) \tag{2}$$

where

$$Z_0^{(D)} = (2\pi\beta)^{-D/2} \tag{3}$$

with D indicating the dimensions of the free motion on to which it is assumed the potential energy $V(\mathbf{r})$ is switched. Equation (2) follows from Eq. (1) with the (usually drastic) approximation that the wave functions are replaced by plane waves in D dimensions while the energy levels are merely shifted by a 'constant' V.

The next step is to set up the differential equation satisfied by Z_{TF}. To do so, dropping the subscript TF for the present for notational convenience; we write from Eq. (2):

$$\nabla Z = (-\beta \nabla V) Z. \tag{4}$$

Differentiating Eq. (4) partially with respect to β then yields

$$\begin{aligned}\frac{\partial \nabla Z}{\partial \beta} &= -Z \nabla V - \beta \nabla V \frac{\partial Z}{\partial \beta} \\ &= -Z \nabla V + \beta Z V \nabla V + \tfrac{1}{2} D Z \nabla V,\end{aligned} \tag{5}$$

the second line following from the use of the explicit form (3).

Rearranging Eq. (5) allows one to write, for the Thomas-Fermi approximation to the Slater sum, the differential equation

$$V \nabla Z + \frac{\partial}{\partial \beta}(\nabla Z) = \left(\frac{D}{2} - 1\right) Z \nabla V. \tag{6}$$

It is to be expected that Eq. (6) will have omitted higher spatial derivatives than the first.

Next we return to Eq. (1) without approximation, but still separating out the free particle motion as in Eq. (3) by writing

$$Z = Z_0^{(D)} f. \tag{7}$$

After forming the quantity $\nabla(\nabla^2 Z)$ directly from Eq. (1), and employing the Schrödinger equation, we find the result which we wish to employ for a potential $V(\mathbf{r})$ corresponding to a uniform electric field, namely

$$\frac{1}{8} \nabla(\nabla^2 Z) - V \nabla Z - \frac{\partial}{\partial \beta}(\nabla Z) + \left(\frac{D}{2} - 1\right) Z \nabla V = 0. \tag{8}$$

which reduces to Eq. (6) when the first term is neglected.

Let us turn immediately to the admittedly simple example where $V(\mathbf{r})$ is generated solely by switching on a constant field of arbitrary strength $\mathscr{E}$ along the z axis. For this case, the result for Z is known and is explicitly[2]

$$Z = (2\pi\beta)^{-3/2} \exp(\beta \mathscr{E} z + \beta^3 \mathscr{E}^2/24). \tag{9}$$

Evidently $\partial^2 Z/\partial z^2 = (\beta\mathscr{E})^2 Z$, and the desired z component of the vector Eq. (8) becomes, with $V = -\mathscr{E}z$:

$$\text{LHS of Eq. (8)} = \frac{1}{8}(\beta\mathscr{E})^2 \frac{\partial Z}{\partial z} + (\beta\mathscr{E}^2) zZ - \frac{\partial}{\partial\beta}(\beta\mathscr{E}Z) - \frac{Z\mathscr{E}}{2}. \tag{10}$$

Using Eq. (9) again to form the β derivative term in Eq. (10) one finds

$$\frac{\partial}{\partial\beta}(\beta\mathscr{E}Z) = Z\beta\mathscr{E}\left(-\frac{3}{2\beta} + \mathscr{E}z + \frac{1}{8}(\beta^2\mathscr{E}^2)\right) + Z\mathscr{E}. \tag{11}$$

Substituting Eq. (11) into Eq. (10) the quadratic and cubic terms in the field immediately cancell. After a brief calculation, the coefficient of the linear term in the field strength $\mathscr{E}$ is found also to be identically zero, verifying that the exact form (9) satisfies Eq. (8), with $D = 3$.

In conclusion, Eq. (8) is the main result of the present work, motivated by the desire to treat atoms and molecules in intense external fields. Equation (8) is shown to be satisfied for free electrons in a constant electric field of arbitrary strength, for which the Slater sum is known to be given by Eq. (9). The generalization of the method outlined in this letter to treat the level spectrum of a hydrogen-like atom in an intense external field will be reported elsewhere.

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